INSTITUTE NOTES.

NOVEMBER, 1940.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

BANGERT, Norman Roy, B.Sc., Chemist, 26, Harrington Square, London, N.W. 1. (*R. G. Stickland ; H. E. Priston*) (*Trans. from Student.*)

BOOKLESS, Douglas Ernest, Works Manager and Director, Petroleum Engineering and Trading Co., Ltd., London. (*N. Matheson ; R. J. Stallard.*)

FOSSETT, Hubert, Engineer, Associated Ethyl Co., Ltd., London. (*F. H. Garner ; S. J. M. Auld.*)

GUNBY, Frank, Tanker Engineer, c/o Anglo-American Oil Co., Ltd.

HOWARD, Frederick George, M.Sc., Chemist, I.C.I., Ltd. (*A. W. Nash ; T. G. Hunter*) (*Trans. from Student.*)

O'CONNOR, Dominie Desmond Taaffe, Production Engineer, Trinidad Petroleum Development Co., Palo Seco, Trinidad. (*H. V. Lavington ; L. K. White.*)

ROBINSON, James Terence Trimble, Refinery Superintendent, Trinidad Leaseholds, Ltd., Point-a-Pierre, Trinidad. (*B. G. Banks ; F. L. Melvill*) (*Trans. from Member.*)

SHORTHOSE, John William, B.Sc., Chemist (Anglo-Iranian Oil Co., Ltd.), 48, Wellington Road South, Hounslow, Middlesex. (*A. E. Dunstan ; F. B. Thole.*)

SMITH, Bernard William, Engineer, British Diesel Oil & Petrol Co. (*G. S. Pound ; Harold Moore.*)

SMITH, Reginald John, Supervisor, Petroleum Depot. (*Trinidad Leaseholds, Ltd.*) (*J. McConnell Sanders ; W. B. Heaton.*)

WILLIAMS, Charles Garrett, M.Sc., A.M.I.Mech.E., Engineer, Shell Refining and Marketing Co. (*J. A. Oriel ; E. Le Q. Herbert.*)

Candidates for Admission as Students.

FARMAIAN, F. M.	The University of Birmingham Dept. of Oil Engineering and Refining.
FELLOWES, M. L.	" " " "
GREEN, S. J.	" " " "
HARTLEY, D. A.	" " " "
JONES, R. E.	" " " "
MORGAN, C. R.	" " " "
OVER, J. R.	" " " "
PEARCE, A. W.	" " " "
SPENCER, F.	" " " "
THURSTON, P.	" " " "

TWINN, G. B. The University of Birmingham Dept. of Oil Engineering and Refining.
WEAVER, A. G. T. " " " "
WHITEHEAD, R. C. " " " "

All the above candidates are proposed by *Prof. A. W. Nash* and seconded by *Dr. A. H. Nissan.*

KEEN, S. Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)
SASSON, A. " " " "

STUDENTS' MEDAL AND PRIZE.

The Council offers a Medal and Prize (to the value of Five Pounds in books) for the most meritorious essay submitted by a Student Member of the Institute on one of the following subjects :

1. Limitations to Deep Drilling.
2. Problems of Water Shut-off.
3. Deep Well Surveying.
4. Theory and Practice of Gas-lift.
5. Theory and Practice of Water Drives.
6. Catalytic Processes for Conversion of Petroleum Fractions.
7. Commercial Utilization of Lubricating Oil Extracts.
8. Recent Developments in Thermal Cracking.
9. The production of high-octane motor spirit.
10. Economy of fuel and lubricants in engines.

Entries must be received by the Secretary of the Institute not later than 1st May, 1941.

The maximum length of the essay is not specified; but generally essays should be from 4,000 to 6,000 words in length.

Entries must be typed, and one carbon copy must be furnished in addition to the original copy. The Council is prepared to give financial assistance to students who experience difficulty in getting their MSS. typed.

BURGESS PRIZE.

Entries are also invited for the Burgess Prize (of value up to Five Pounds in books) for an essay dealing with some aspect of the economics of the petroleum industry, including the transport and distribution of petroleum products.

The conditions of entry for the Burgess Prize are the same as for the Students' Medal and Prize.

The Council reserves the right to withhold the award of either of these prizes, or to award prizes of such lesser value as it may decide.

NOMINATIONS FOR COUNCIL.

Every Fellow, Member or Associate Member of the Institute may send in writing to the Council the name of a Fellow or Member whom he desires to recommend for election to the Council. This nomination must be signed by at least nine other Fellows, Members or Associate Members, and delivered to the Secretary not later than 31st December, 1940. No member may sign more than one Nomination Paper. Nomination papers may be obtained from the Secretary.

ARTHUR W. EASTLAKE,
Honorary Secretary.

Vol. 26. No. 205. November 1940.

THE CLEMENT–PIGNEGUY KNOCK INDICATOR.*

By D. M. Clement and P. G. Pigneguy.†

Synopsis.

A long-felt need in engine-fuel testing has been an indicator of knock intensity which is unaffected by combustion pressure and one also in which the accurate functioning does not rely on the interdependent setting of its component parts.

The indicator described in this paper is shown to possess the desired qualities, which enables testing to be carried out over the entire octane scale without alteration of the original setting. While the construction may appear to be on similar lines to the A.S.T.M./C.F.R. bouncing-pin indicator, the change in principle involved is fundamental.

The new indicator has so far only been used in the standard C.F.R. engine and also a high-speed C.F.R. engine, but it is felt that the principle can be successfully adapted for full-scale car and aero-engine testing.

In the anti-knock rating of fuels it is well known that the C.F.R. engine is in considerable use and has shown itself reasonably reliable. If criticism can be made against any particular part of it, that part is the bouncing-pin, which is a source of direct error in the rating of fuels. This apparatus is the medium by which the knock intensity in the engine is registered quantitatively as a knock-meter reading. As is known, the method of fuel rating is by comparing two known fuels against the unknown sample, the comparison being effected by the use of the knock-meter readings. Should these knock-meter readings not be truly representative of the knock intensity occurring in the engine on the various fuels, then an immediate error in rating is made.

Investigation has been carried out for some time past on the actual physical phenomena which take place in the Standard A.S.T.M./C.F.R. bouncing-pin. The knock indicator described in this article has been designed to overcome certain faults inherent in the operation of the standard apparatus.

A brief outline of the standard C.F.R. bouncing-pin apparatus is as follows :—

A steel pin about 7 in. in length and $\frac{1}{4}$ in. diameter rests in a vertical position on a diaphragm, the diaphragm and pin being supported in the main body, which is screwed into the engine cylinder. On top of the main body is an assembly of two leaf-spring contacts and a bumper spring mounted one above the other. The lower leaf-spring contact rests on the pin-top and exerts sufficient pressure on it, to hold the pin against the diaphragm during normal combustion of the engine. Above this lower leaf-spring contact separated by about a 0·003-in. gap is the upper leaf-spring contact arranged in a buffer system with a plunger and spring sliding in a guide. This upper leaf-spring and plunger may be adjusted to vary the gap between the two contacts, and they arrest the motion of the lower contact without shock, when it is driven up by detonation, so that an impulse of current flows in the circuit through the contacts. The

* Paper received 24th September, 1940.

† "Shell" Refining & Marketing Co., Central Laboratories, London.

time of contact is registered on the knock-meter as a mean value of current flowing.

Under detonating conditions the steel bouncing-pin is driven off the diaphragm by the impact of detonation and is brought to rest by the retarding forces of the lower leaf-spring and the action of closing the contacts. The pin has thus partly stored its energy of upward movement in the resilience of the lower leaf-spring, and this member returns the pin to the diaphragm with such a velocity that it rebounds and the process is repeated. Thus for one knock impact in the engine cylinder, the pin is set into a state of oscillation. The frequency of this oscillation is dependent on the pressure on the pin downward and the mass of the pin itself. With the normal setting of the standard pin the frequency is of approximately 800 cycles per second. With a very light lower leaf-spring pressure this vibration may continue throughout the engine cycle until the next detonation occurs. Under normal leaf-spring pressure the vibration dies away well before the commencement of the next engine cycle.

It is important to note now what is occurring to the diaphragm while this vibration of the pin upon it is taking place. Its vertical deflection is altering according to the pressure in the cylinder. Thus, as the knock impact is being recorded by the vertical travel of the lower contact under the action of the vibrating pin, it may well be that the time of closure of the contacts is due more to the combustion pressure in the cylinder than to the rapid vibration of the pin set up by detonation. The effect of combustion pressure being recorded as detonation is more troublesome at the higher compression ratios where the deflection of the diaphragm due to higher combustion pressures is much greater. For example :—

In recent experiments it was determined that when an engine was not detonating, a considerable deflection of the diaphragm took place, due to combustion pressure : this was found to be 0·0015 in. at 4 : 1 compression ratio, 0·0025 in. at 8 : 1 compression ratio, and the diaphragm deflection plotted against compression ratio was almost exactly a straight line. With this evidence it is clear that, when the engine is being run on any non-detonating fuel, if this diaphragm deflection curve rises above the leaf-spring contact clearance, a reading on the knock-meter is recorded due to combustion pressure. (A detailed account of this experimental work and fundamental theory underlying it is given later in this paper (Appendix A).)

It was also determined that with a normal pressure downwards on the pin by the lower leaf-spring, the pin remained in contact with the diaphragm when no detonation was present.

Fig. 1 shows the displacement of the diaphragm, on which is superimposed the movement of the lower leaf-spring contact, under the action of the vibrating pin. It was evident that when a standard bouncing-pin was set with a contact gap of 0·003 in., part of the closure of the gap was due to combustion pressure, and the rest due to the oscillation of the pin and lower leaf-spring caused by detonation. As expected, it was determined that the bouncing-pin contacts closed three to four times per engine cycle (see Fig. 2).

Owing to the smaller deflection of the diaphragm shortly after combustion when the gases begin to expand, the recording of the oscillation

on the standard bouncing-pin is masked after the first three or four vibrations.

Thus the standard bouncing-pin records only a portion of the vibration or oscillation due to detonation, and in the case of a heavier detonation

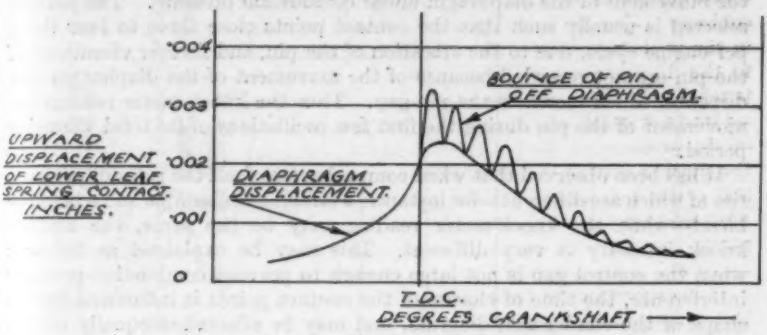


FIG. 1.

the pin relies on a wave of larger amplitude to increase the time of contact and thus increase the knock-meter readings.

If the standard pin could be relied upon to record the same number of vibrations on all fuels—*e.g.*, the first three—without any influence due to combustion pressure, then the knock-meter readings would be comparative for the degree of detonation in the engine.

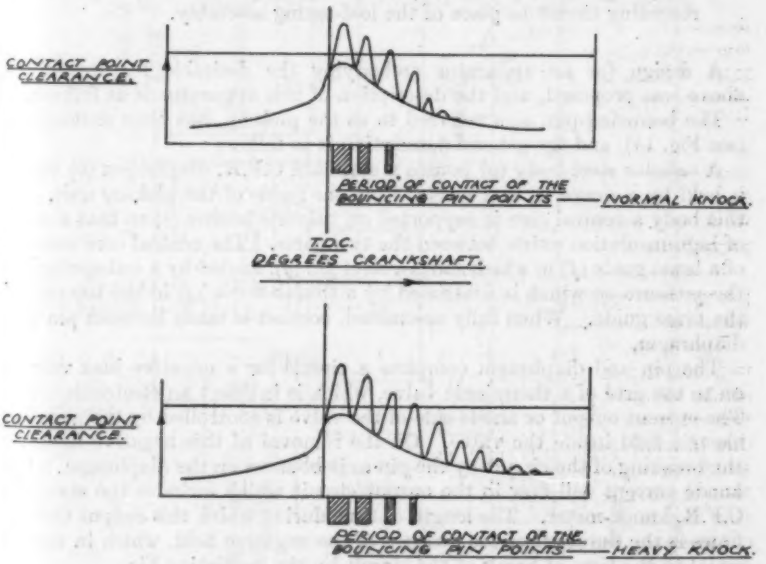


FIG. 2.

The foregoing criticism of the standard C.F.R. bouncing-pin may be summarized as follows :—

The knock-meter readings being proportional to the duration of contact of the points, activated by the pin movement, are always influenced by the movement of the diaphragm under combustion pressure. The pin-gap selected is usually such that the contact points close three to four times per engine cycle, due to the vibration of the pin, and further vibrations of the pin are not recorded because of the movement of the diaphragm in a direction which increases the pin-gap. Thus the knock-meter records the movement of the pin during the first few oscillations of its total vibrating period.

It has been observed that when comparing two fuels the rates of pressure rise of which are different—for instance, a straight-run sample and a benzene blend—while the knock-meter reading may be the same, the audible knock intensity is very different. This may be explained as follows : when the control gap is not large enough to prevent combustion-pressure interference, the time of closure of the contact points is influenced by the shape of the combustion diagram, and may be affected unequally on the two fuels by combustion, depending on the broadness of the peak of the diagram, quite apart from the detonation wave accompanying it.

From the foregoing analysis, advantageous changes in the design of the pin and recording circuit were made, and are as follows :—

1. Recording all pin movement *relative* to the diaphragm.
2. Measuring by an extremely small current the time of bounce of the pin *off* the diaphragm, by including the pin and diaphragm in the recording circuit in place of the leaf-spring assembly.

A design for an apparatus embodying the desirable features given above was proposed, and the description of this apparatus is as follows.

The bouncing-pin, now referred to as the pick-up, has been re-designed (see Fig. 14), and the general description is as follows :—

A tubular steel body (*a*) houses a standard C.F.R. diaphragm (*b*) which is held by a sleeve (*c*) and nut (*d*) from the inside of the pick-up unit. In this body a central core is supported on bakelite bushes (*e*) so that a state of high insulation exists between the two parts. The central core consists of a brass guide (*f*) in which slides a steel pin (*g*), loaded by a coil-spring (*h*), the pressure on which is controlled by a thumb-screw (*j*) in the top end of the brass guide. When fully assembled, contact is made between pin and diaphragm.

The pin and diaphragm complete a circuit for a negative bias voltage on to the grid of a thermionic valve, which is in effect an electronic relay. The current output or anode side of the valve is controlled by the negative electric field inside the valve. On the removal of this negative field, by the breaking of the circuit by the pin as it bounces on the diaphragm, a full anode current will flow in the output circuit which includes the standard C.F.R. knock-meter. The length of time during which this output current flows is the duration of the absence of the negative field, which in turn is equal to the time of break of the circuit by the oscillating pin.

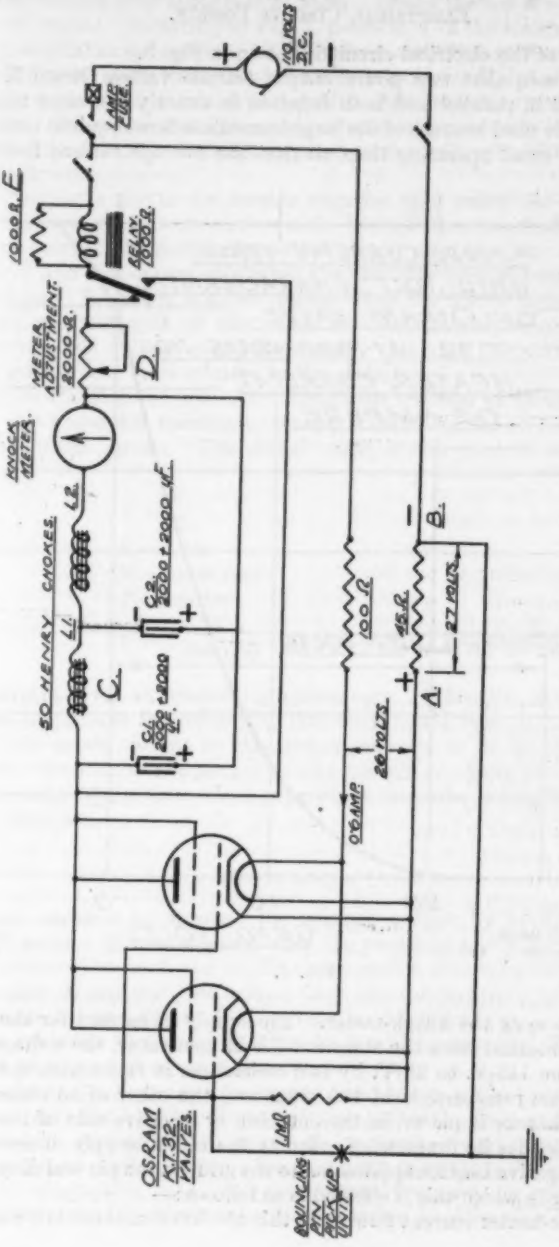


FIG. 3.

CLEMENT–PIGNEGUY KNOCK INDICATOR. CIRCUIT DIAGRAM—SUITABLE FOR USE WITH COIL OR MAGNETO IGNITION C.I.E. ENGINE.

Electrical Circuit Design.

A diagram of the electrical circuit is shown in Fig. 3.

It will be seen that two power output tetrode valves Osram K.T. 32 are connected in parallel and both function in exactly the same manner. Two valves are used because of the large immediate flow required under the conditions of small operating time, so that the average current flowing is

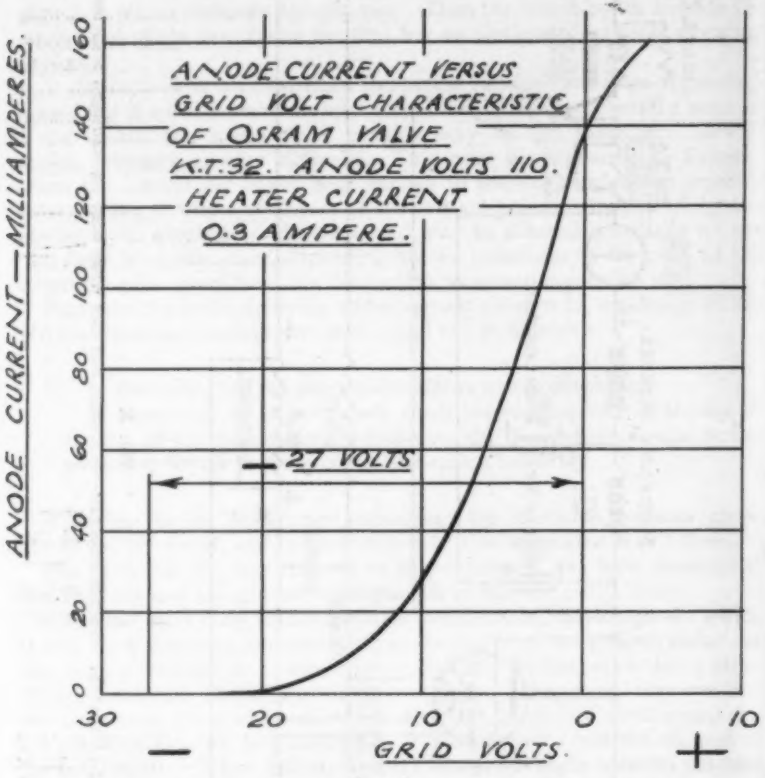


Fig. 4.

sufficient to work the knock-meter. The supply of current for the valve-heaters is obtained from the standard C.F.R. generator, the voltage being reduced from 110 V. to 26 V. by two resistances in series with the valve-heaters. One resistance is of 100 ohms and the other of 45 ohms. The 45-ohm resistance is placed in the outgoing or negative side of the valve-heaters. Besides its function of reducing the 110-V. supply, it serves as a source of negative bias for application to the grid via the pin and diaphragm. The manner in which this is effected is as follows :—

The valve-heater current flowing in this 45-ohm resistance is 0·6 ampere,

thus the voltage drop along it is 27 volts. (From the law $E = RI = 45 \times 0{\cdot}6 = 27$ volts.) Referring to Fig. 3, position *A* of the resistance is at the same potential as the cathodes of the valves, and thus, as there is a voltage drop of 27 volts along the resistance to *B*, the position *B* is of lower potential than *A*, or, in other words, it is negative with respect to the cathodes by 27 volts. From the grid volt/anode current characteristic (Fig. 4) it can be seen that this 27 volts when applied to the grid will reduce the anode current flowing to zero.

This action is due to the intense negative field inside the valve, which stops the passage of electrons across the space between cathode and anode. Thus no current can flow in the output circuit until this bias is completely removed, and this occurs only when the circuit is broken between pin and diaphragm. To ensure a stable output when the above circuit is broken, the cathode and grid of the valve are permanently connected by a 1-megohm (one million ohms) resistance; this fixes the working position of the grid at zero volts relative to the cathode.

Thus in the state of rest of the apparatus the bias of 27 volts is acting across the 1-megohm resistance, causing a small current to flow in the pin and diaphragm circuit. The actual value of this current is 0·027 milliampere.

$$I = \frac{E}{R}$$

where E = volt
R = resistance
I = current.

$$\therefore \quad I = \frac{27}{1{,}000{,}000} \text{ amperes} = 0{\cdot}027 \textit{ milliampere.}$$

This current is for all practical purposes zero. When the circuit between pin and diaphragm is broken, the bias on the grid rises to zero, and this allows the anode current to rise instantaneously to its maximum value. Thus the vibration of the pin previously referred to allows anode or output current to flow for a time which is precisely the same in length and nature as the vibration.

The Knock-meter Circuit.

It now remains to measure the average output by applying it to a suitable meter. It was required that the standard knock-meter (without heater element) be used, and as this instrument is a moving-coil meter with no damping of any sort, the output from the valves has to be electrically damped to deliver a steady D.C. current to the meter.

With reference to the circuit Fig. 3c, it will be seen that this damping consists of a network of capacity and inductance.

The effect of inductance is to oppose any change in the value of current flowing; capacity has the effect of storing current. Thus in the arrangement shown, assuming the current to be rising, inductance L1 offers a large resistance to the current; C1, which is a capacity of 2000 or 4000 μF, offers an alternative path, and the current flows into it and is stored. The inductance L1, however, will not resist all the rapidly changing

current, and, whatever current passes, it meets a similar inductance and capacity L2 and C2 with the meter in series. Capacity C2 is charged, and the meter registers a reading. Now, if the current is cut off at the source, C1 and C2, being charged with a definite amount of current, now discharge through the meter—*i.e.*, in the same direction as the original current—and thus the constancy of the reading is maintained.

In the case of the output from the valve, which is a rapidly pulsating supply (when detonation is being measured), the condensers at each interval between pulsations discharge the correct amount to maintain a constant reading on the meter.

The surges of current in the meter circuit are illustrated graphically, with an accompanying explanation, in Appendix B.

The current passing through the meter to the anodes of the valves is also passed through a variable resistance *D* of 2000 ohms and a relay *E*.

Resistance *D* allows of adjustment to the anode supply voltage so as to vary the meter reading as required.

Relay *E* is a magnetic relay with one break and one make contacts. The reason for its inclusion in the circuit may be explained as follows :—

The output of the set through the meter and relay is controlled by the time of absence of the negative grid bias. Should the wires connecting the set to the pin on the engine be accidentally parted, the meter would be damaged by the high current which would flow. With the relay in circuit, when the current flowing rises to a value slightly in excess of that required for full-scale meter reading—*i.e.*, 2 milliamperes—the relay operates and opens the circuit through the meter and by-passes the current straight through to the valves. The relay locks itself in this position, thus safeguarding the meter, until it is released by the action of again completing the negative bias circuit.

The set has been found to give sufficient output at a supply voltage of 110 volts from the D.C. generator, which is part of C.F.R. equipment. The total power required is 0·6 ampere at 110 volts = 66 watts. The set operates satisfactorily on either coil or magneto ignition engines; there are several minor checks to the wiring, however, when first fitting the apparatus to the engine. These are as follows :—

Engine with magneto ignition.

Check that there is no earth on the positive pole of the generator.

Engine with coil ignition.

1. The end of the 500-ohm resistance in the coil ignition circuit must be transferred from the negative pole of the generator to the positive.

2. The earth on the positive pole of the generator must be removed and the earth placed on the negative pole.

The essential point in both cases is to ensure that no earth exists on the positive pole of the generator, because the negative pole is earthed when the set is operating correctly, and thus a direct short circuit on the generator must be avoided.

The following performance is claimed for this apparatus :—

(*a*) The apparatus measures the true knock intensity over the

entire testing range of octane numbers without any change of original setting.

(*b*) Combustion pressure effects are not recorded. If the engine is run on 100-octane fuel at the compression ratio giving standard knock intensity, with the knock-meter reading at mid-scale, and the fuel is then changed over to pure benzene, the knock-meter reading will fall away to zero even though the fuel is " bumping " quite heavily.

(*c*) The operation of the apparatus is more simple than that of the standard pin.

(*d*) The sensitivity per octane number is controllable. 10 knock-meter divisions per octane number is practicable.

(*e*) The current, 0·027 milliampere, is so small that there can be no trouble due to arcing at the point of contact between pin and diaphragm.

(*f*) The apparatus can be fitted in a quarter of an hour to operate satisfactorily from the D.C. generator on either coil or magneto ignition C.F.R. engines.

(*g*) Maintenance of the set should be negligible. New valves may be required at intervals of two years. Cleaning of the pick-up unit should be carried out at the same time as decarbonizing the engine—*i.e.*, approximately every 100 hours running time.

The authors wish to thank the Asiatic Petroleum Co., Ltd., and Shell Refining and Marketing Co., Ltd., for permission to publish the results of the experimental work described, which was carried out in the Company's research laboratory in London.

APPENDIX A.

Detailed Experimental Investigation on Motion of Standard Bouncing-Pin.

An apparatus called the Weidenhoff distribuscope which was designed to measure the time of make and break of the contact points of automobile ignition distributors was used to study the movement of the contact points of the standard bouncing-pin. The duration of contact of the points is indicated on a circular scale of degrees by the flashing of a neon lamp which is incorporated in the rotating arm of the distribuscope. By rotating the arm at a speed synchronous with the engine speed, the duration and number of contacts of the bouncing-pin points during one engine cycle can be readily estimated.

The shaded diagrams on the drawing Fig. 5 A and B represent the periods of contact, on crankshaft degree scale, for various bouncing-pin contact point clearances at 5·3 : 1 and 8·0 : 1 compression ratio respectively. Diagram *X* represents contact time on the detonating fuel, and diagram *Y* non-detonating fuel, the latter therefore showing interference due to combustion pressure. For standard knock intensity at 5·3 to 1 compression ratio (C.R.) on a 65-octane-number fuel, the contact points usually close three times. On reducing the gap from 0·004 in. to 0·0025 in. the closure of the contact points is due to the sum of the deflection of the diaphragm

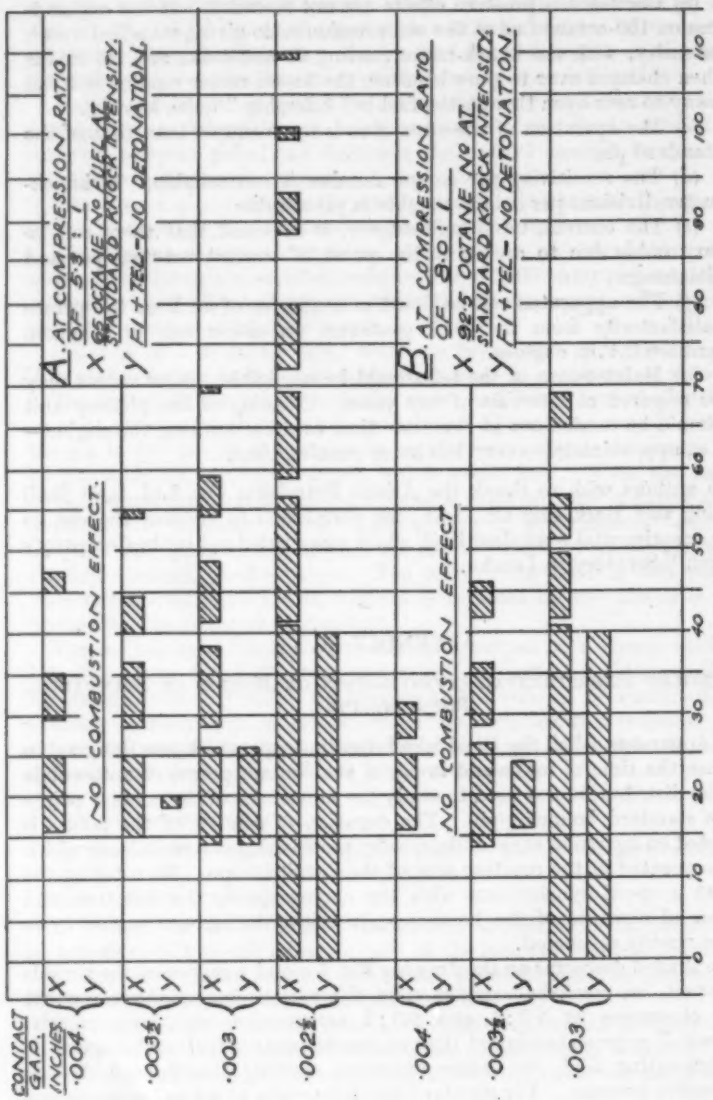

CONTACT GAP. INCHES
·004.
·003½.
·003.
·002½.
·004.
·003½.
·003.
X
y
A. AT COMPRESSION RATIO OF 5·3 : 1
NO COMBUSTION EFFECT.
X 65 OCTANE No FUEL AT STANDARD KNOCK INTENSITY.
y E1 + TEL – NO DETONATION.
B. AT COMPRESSION RATIO OF 8·0 : 1
NO COMBUSTION EFFECT
X 92·5 OCTANE No AT STANDARD KNOCK INTENSITY.
y E1 + TEL – NO DETONATION.
0
10
20
30
40
50
60
70
80
90
100
110
DURATION OF CONTACT OF PIN POINTS.
DEGREES CRANKSHAFT.

FIG. 5.

caused by combustion pressure and the induced vibrations of the pin caused by detonation. When the gap is less than the deflection of the diaphragm caused by combustion pressure, the knock-meter does not record true detonation effect.

At a C.R. of 8 : 1 and pin-gap of 0·003 in. (see Fig. 5B) the duration of contact of the points is greater than that at the C.R. of 5·3 : 1 when the engine is running on the same fuel. This observation confirms that the movement of the lower contact caused by the deflection of the diaphragm increases with an increase in compression ratio.

It was found when an engine was not detonating that a deflection of the diaphragm took place amounting to 0·0015 in. at a compression ratio of 4 : 1 and 0·0025 in. at 8 : 1 C.R. due to combustion pressure. It was determined that under these non-detonating conditions the pin remained on the diaphragm throughout the cycle at all compression ratios, provided that there was a normal pressure downwards by the lower leaf-spring. This was carried out by insulating the pin in its guides and completing the circuit through the pin and diaphragm and through the neon tube referred to above. If the spring pressure was insufficient there was a bounce of the pin due to combustion when toluene, benzene, and aromatic fuels were used, although there was no detonation.

The total period of make of the bouncing-pin contacts caused by detonation has a duration of about 15° crankshaft when the gap is set to 0·004 in. Frictional losses and other damping cause the pin eventually to come to rest before the end of the engine cycle.

Diagrams of pin movement were also observed with the aid of the Standard–Sunbury cathode-ray oscillograph. These diagrams are reproduced in Fig. 6. The vertical and horizontal axes represent displacement and time respectively. Although they carry no scale, they are all relative in size to one another. These were obtained by placing a magnetic pick-up above a steel lower-leaf spring resting on the pin-top. Thus movement of the spring was recorded.

Fig. 6B shows the leaf-spring contact movement at standard knock intensity on 65 O.N.–5·3 : 1 C.R.

Fig. 6A—leaf-spring contact movement at 5·3 : 1 C.R. when running on non-detonating fuel—*i.e.*, no vibration of pin.

Fig. 6F standard knock intensity at approximately 8 : 1 C.R. on 92·5 octane fuel.

Fig. 6E leaf-spring contact movement at 8 : 1 C.R. when running on non-detonating fuel. Note the relative position of diaphragm or leaf-spring deflection at 65 O.N. setting Fig. 6A (non-detonating).

Thus, while it can be seen that the vibration of the pin when detonation is occurring is approximately of the same nature and amplitude at both 5·3 : 1 and 8 : 1 C. Ratios; in the case of Fig. 6F—that is, when at standard knock intensity on 92·5 octane fuel—the vibration is displaced vertically under the action of the diaphragm deflection.

By increasing the thickness of the diaphragm from the standard 0·015 in. to 0·025 in. the deflection by combustion pressure is greatly reduced. At the same time the vibrations of the pin due to detonation have approximately the same amplitude. Diagrams 6 D, C, H and G are the corresponding diagrams with the thicker diaphragm.

DEGREES CRANKSHAFT.

FIG. 5.

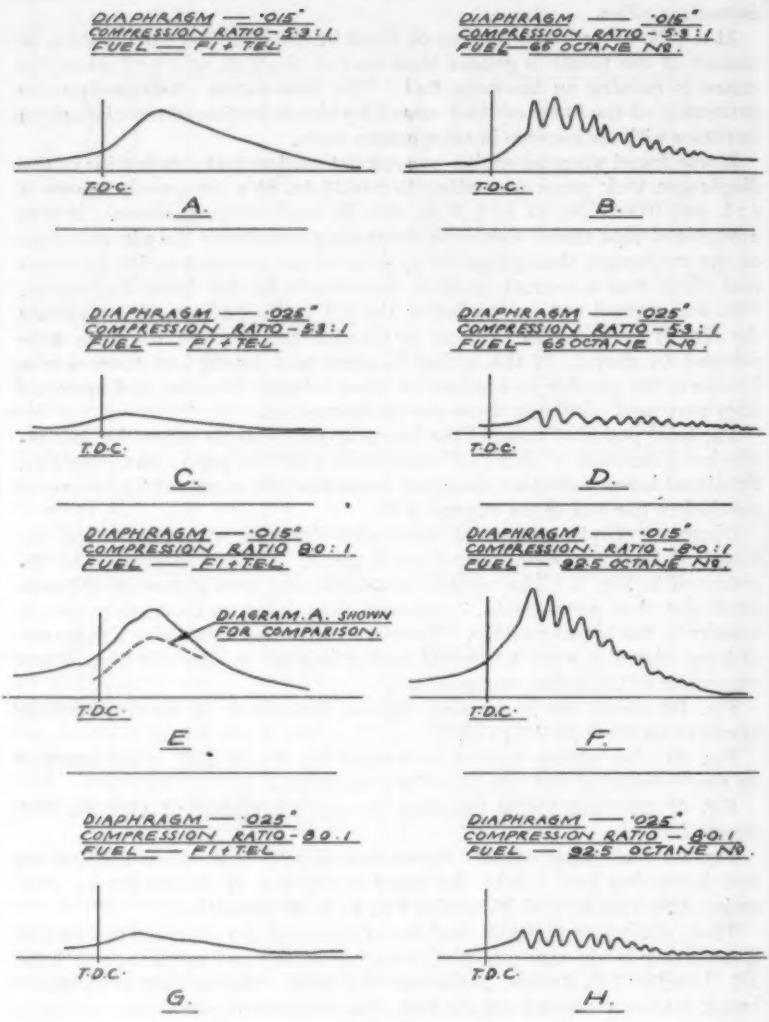

DIAPHRAGM — ·015"
COMPRESSION RATIO - 5·3 : 1
FUEL — FI + TEL
T.D.C.
A.
DIAPHRAGM — ·015"
COMPRESSION RATIO - 5·3 : 1
FUEL — 65 OCTANE NO.
T.D.C.
B.
DIAPHRAGM — ·025"
COMPRESSION RATIO - 5·3 : 1
FUEL — FI + TEL
T.D.C.
C.
DIAPHRAGM — ·025"
COMPRESSION RATIO - 5·3 : 1
FUEL — 65 OCTANE NO.
T.D.C.
D.
DIAPHRAGM — ·015"
COMPRESSION RATIO 8·0 : 1
FUEL — FI + TEL
DIAGRAM A. SHOWN FOR COMPARISON.
T.D.C.
E.
DIAPHRAGM — ·015"
COMPRESSION RATIO - 8·0 : 1
FUEL — 92·5 OCTANE NO.
T.D.C.
F.
DIAPHRAGM — ·025"
COMPRESSION RATIO - 8·0 : 1
FUEL — FI + TEL
T.D.C.
G.
DIAPHRAGM — ·025"
COMPRESSION RATIO - 8·0 : 1
FUEL — 92·5 OCTANE NO.
T.D.C.
H.

FIG. 6.

Thus, although the diaphragm is much thicker, the energy transmitted to the mass of the pin has not been materially reduced. Reference is made to this important and interesting fact in the following discussion.

Discussion on the Response of the Clement–Pigneguy Bouncing-Pin to Knock Intensity.

It is obvious that the mechanics of the standard bouncing-pin are identical with those of the C.P. pin. The mass of the pin and the spring tension applied to it are closely similar.

Thus any reasoning based on experimental data obtained with the standard apparatus can, within the limits of experimental error, be applied to the C.P. pick-up unit. That this is so is borne out by the several identical characteristics possessed and obtained experimentally by them.

Non-linearity of Knock-meter Readings with Change in Knock Intensity.

It has been determined that with either the standard pin or the C.P. pin the knock-meter readings recorded do not change in proportion with regular changes of octane number when the engine is running at a fixed compression ratio. While the non-linearity is not serious when the spread of octane number during testing is considered, *i.e.*, approximately 4 octane number, it is interesting to investigate why the non-linearity should exist at all. In the following work and proofs it is shown that the non-linearity is not due to the knock-meter indications being non-linear with the knock occurring in the engine, but it is due to the fact that the *actual knock in the engine* is not linear with variation of octane number.

The increase in engine knock is not linear with decrease in octane number, and tends to increase very rapidly (probably something near square law) as the knock becomes heavy.

In the work of examining the movements of the standard C.F.R. pin, much assistance was derived from the Weidenhoff Distribuscope, details of which have already been given. The bouncing-pin was insulated in its guides and an electrical circuit completed through the pin and diaphragm and through the distribuscope. Under a normal spring pressure on the pin, when detonation occurred, the distribuscope showed a vibration or series of regular breaks in the circuit between pin and diaphragm. This vibration was of approximately 800 cycles per second, and the pin completed about 9 or 10 cycles for each detonation of the engine.

These 9 or 10 cycles start wide (showing the pin off the diaphragm a long time), and taper away to zero with a slight increase in frequency. It is important to note that these oscillations of the pin fall to zero before the next knocking combustion of the engine. It is the total time that the pin is vibrating off the diaphragm which we wish to measure. The reasons for this can be shown in an approximate mathematical proof as follows :—

From the law Kinetic Energy = Work Done.

Some of the kinetic energy of the detonation does work in driving the mass of the bouncing-pin against the force of the lower leaf-spring pressure and its own weight :—

thus
$$\frac{WV^2}{2g} = FS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W = weight of pin, V = velocity of pin, g = gravitational acceleration 32·2 *feet per second, per second*, F = force retarding-pin, S = distance pin moves in coming to rest.

The various figures measured on the standard pin were as follows :—

F = lower leaf-spring pressure (assumed to remain constant although it is deflected slightly) plus pin weight

$$= 210 + 33 \text{ gm.} = \frac{210 + 33}{454} \text{ lb.} = \frac{243}{454} \text{ lb.}$$

W = weight of pin = 33 gm. $= \frac{33}{454}$ lb.

S = the actual distance moved by the pin under detonation measured with the aid of Vernier gap adjustment.

$$= 0{\cdot}0005 \text{ in.} = \frac{0{\cdot}0005}{12} \text{ ft.}$$

therefore from $\frac{WV^2}{2g} = FS$

$$V^2 = 64{\cdot}4 \times \frac{243}{454} \times \frac{0{\cdot}0005}{12} \times \frac{454}{33}$$

$$\therefore \quad V = 0{\cdot}15 \textit{ feet per second.}$$

This is the velocity of the pin immediately after the impact of detonation on the diaphragm.

Now from the law $$Ft = \frac{W}{g} . V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where F = force retarding-pin, t = time for pin to come to rest, W = weight of pin, g = gravity, V = initial velocity (as obtained).

$$\therefore \quad t = \frac{W}{g} \cdot \frac{V}{F} = \frac{33}{454} \times \frac{0{\cdot}15}{32{\cdot}2} \times \frac{454}{243}$$

$$= 0{\cdot}00064 \textit{ second.}$$

This is the time for the pin to come to rest off the diaphragm, thus total time for one complete oscillation

$$= 2t = 2 \times 0{\cdot}00064$$
$$= 0{\cdot}00128 \textit{ second.}$$

The pin having thus returned to the diaphragm, it has still considerable energy which is stored in the resilience of the diaphragm ; it is thus thrown off again, and oscillates at the natural frequency of the pin system. This frequency can be calculated from our results above :—

$$\text{frequency} = \frac{1}{T} = \frac{1}{2t} = \frac{1}{0{\cdot}00128} = 780 \text{ cycles per second.}$$

This calculated frequency coincides very closely with the frequency of 800 cycles per second measured on the Weidenhoff Distribuscope, proving

that our approximate calculations are correct in principle. The following conclusions can be reached from this proof :—

$$\text{Kinetic energy of detonation } K = \frac{WV^2}{2g} \text{ given to pin} \quad . \quad (1)$$

This can be re-written in the form :—

$$K \times \frac{2g}{W} = V^2 \text{ or } V = \sqrt{K \times \frac{2g}{W}}$$

and from equation (2)

$$F.t. = \frac{W}{g} . V$$

inserting in (2) the value for V obtained from (1)

$$\therefore \qquad t = \frac{W}{gF}\sqrt{K \times \frac{2g}{W}}$$

$$\therefore \qquad t = \frac{1}{F} \times \sqrt{\frac{2W}{g}} \times K = \frac{1}{F}\sqrt{\frac{2W}{g}} \times \sqrt{K}$$

but for any particular pin setting F, W, and g are constants and can be expressed as C and therefore t can be written :—

$$t = C\sqrt{K}$$

or $$t \text{ } \textit{is proportional to} \text{ } (K)^{\frac{1}{2}}$$

In words, the time the pin is off the diaphragm is proportional to the square root of the kinetic energy of the impact of detonation given to the pin.

A curve to this equation has been drawn (see Fig. 7).

The next important point—does the radio set output current vary in proportion to the time of break of the pin and diaphragm circuit. This point has been accurately checked in the following manner :—

A toothed wheel was obtained and a brush-gear was mounted so as to make good contact with each tooth as the wheel was made to rotate. The wheel was then marked out into 9 parts, and plates were made so that when fixed in position on the wheel they each blanked off a number of the teeth of the wheel. Thus as the wheel rotated a definite number of teeth could be left unblanked, and therefore a definite time of break at the brush could be generated, providing only that the wheel speed was constant. The wheel used has 96 teeth, and 8 of the plates blanked off 10 teeth each. Other plates were provided which made it possible to have open 5 teeth or any multiple of 5 teeth. Thus the contact time could be varied in steps of 5 teeth from 5 up to 90, and finally 96 teeth.

The speed of the wheel was selected at 500 r.p.m. so as to generate a make and break of the circuit similar to the bouncing-pin vibration.

Thus 96 breaks per revolution at 500 r.p.m.

$$= \frac{500 \times 96}{60} \text{ breaks per second.}$$

$$= 800 \textit{ per second.}$$

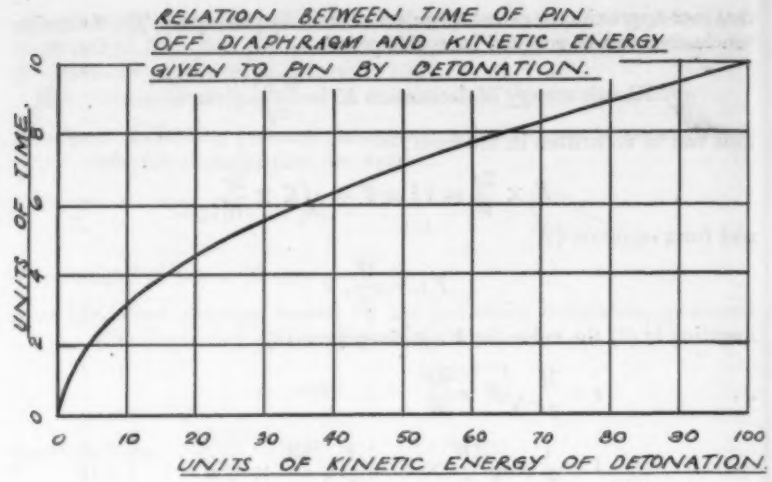

RELATION BETWEEN TIME OF PIN OFF DIAPHRAGM AND KINETIC ENERGY GIVEN TO PIN BY DETONATION.
UNITS OF TIME.
0
2
4
6
8
10
0 10 20 30 40 50 60 70 80 90 100
UNITS OF KINETIC ENERGY OF DETONATION.

Fig. 7.

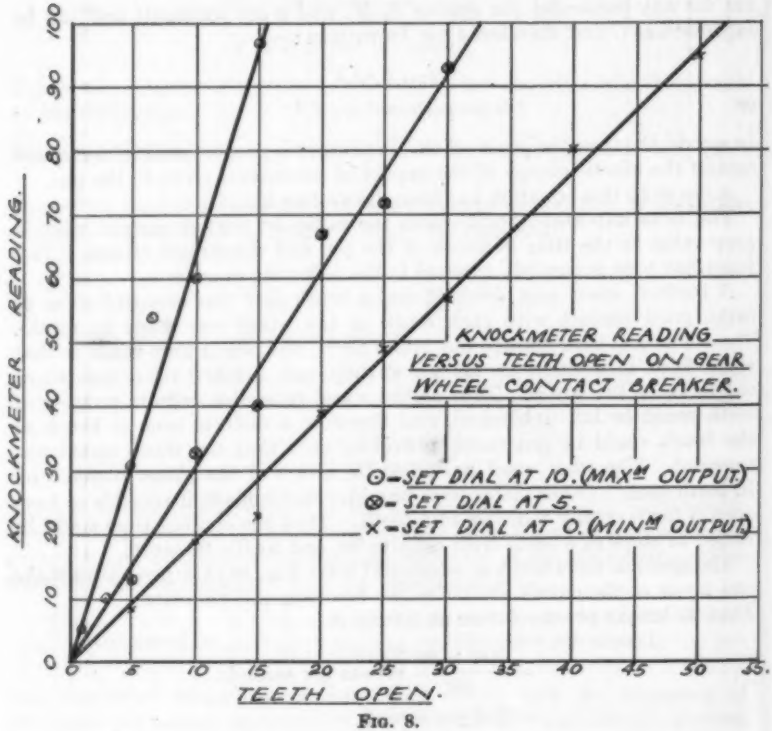

KNOCKMETER READING.
0 10 20 30 40 50 60 70 80 90 100
0 5 10 15 20 25 30 35 40 45 50 55
TEETH OPEN.
KNOCKMETER READING VERSUS TEETH OPEN ON GEAR WHEEL CONTACT BREAKER.
⊙-SET DIAL AT 10. (MAXM OUTPUT)
⊗-SET DIAL AT 5.
×-SET DIAL AT 0. (MINM OUTPUT)

Fig. 8.

The circuit through the wheel was taken to the radio set in place of the pick-up unit, and the knock-meter readings noted as the plates referred to above were removed. Fig. 8 shows the straight-line response of the meter readings with regular change in circuit break time, at three set outputs—minimum, medium, maximum.

As a matter of interest the curves in Fig. 8 have been redrawn in Fig. 9 and instead of the abscissa being "teeth open," the contact times for the

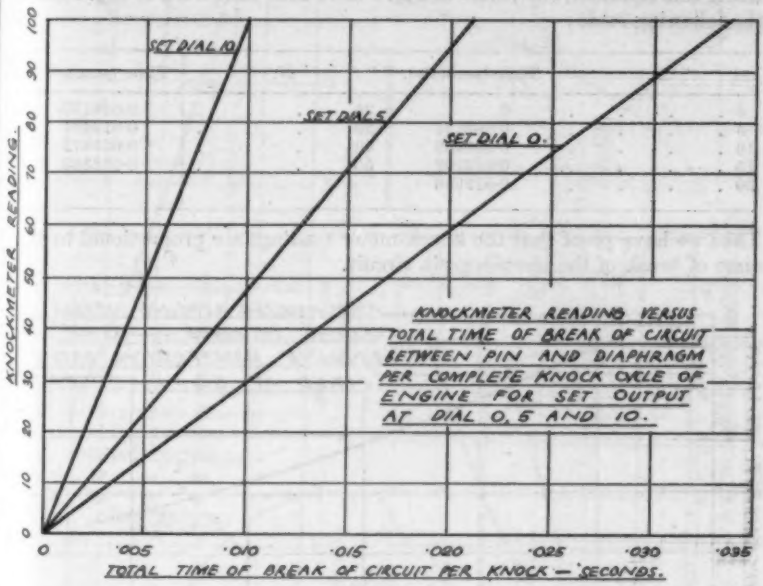


FIG. 9.

teeth have been accurately measured and the calculations involved are as follows :—

To find total time of break of circuit per minute

Wheel running at 500 r.p.m.

Total angle run through per minute

$$= 500 \times 360 \text{ degrees}$$
$$= 3000^\circ \text{ per second}$$

1 tooth-space was accurately measured as giving a break of $1\frac{1}{4}^\circ$.

Now 1° is moved through in $\frac{1}{3000}$ second.

∴ total time of break of circuit per revolution

$$= N \text{ teeth} \times 1\tfrac{1}{4}^\circ \times \tfrac{1}{3000} \text{ seconds.}$$

∴ Total time of break of circuit per minute

$$= N \times 1\tfrac{1}{4} \times \tfrac{1}{3000} \times 500 \text{ seconds}$$
$$= N \times \tfrac{1}{24} \textit{ seconds per minute}$$

where N is the number of teeth left open on the wheel.

It is convenient to express this time, however, in some term relative to the C.F.R. engine; thus as the speed is 900 r.p.m. of the engine, there are 450 theoretical knock impacts per minute. Thus it is perhaps better to express the break of the circuit as :—

Time of break of circuit per knock of engine

$$= N \tfrac{7}{24} \times \tfrac{1}{450} = 0{\cdot}0006468\ N \text{ seconds.}$$

Using this equation, the values in Fig. 8 have been converted to Fig. 9 from the following table :—

N.	Time (seconds).	N.	Time (seconds).
0	0	25	0·016170
5	0·003234	30	0·019404
10	0·006468	40	0·025872
15	0·009702	50	0·032340
20	0·012936		

Thus we have proof that the knock-meter readings are proportional to the time of break of the bouncing-pin circuit.

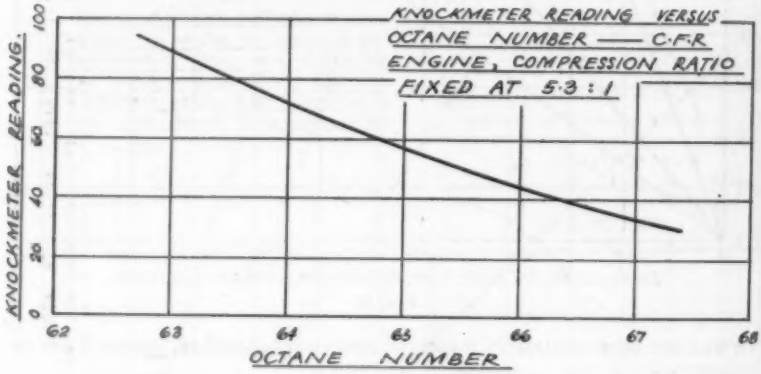


Fig. 10.

As we have already shown, the time the pin is off the diaphragm is a function of the $K\frac{1}{2}$, where K is the kinetic energy of detonation given to the pin; thus Fig. 7 also represents the change in knock-meter reading with change of kinetic energy given to the pin.

Now, the important point is, if the change in kinetic energy of detonation *in the engine* were linear with change in the octane number of the fuel (at a fixed compression ratio), then Fig. 7 would also represent the curve of knock-meter reading versus octane number at the fixed compression ratio.

With the above statement in mind, Fig. 10 was obtained in the following manner :—

The engine was run under standard 65-octane-number conditions and the knock-meter reading set to mid-scale. Then, with no alteration in compression ratio, the engine was run on fuels of various octane number and the knock-meter readings were taken.

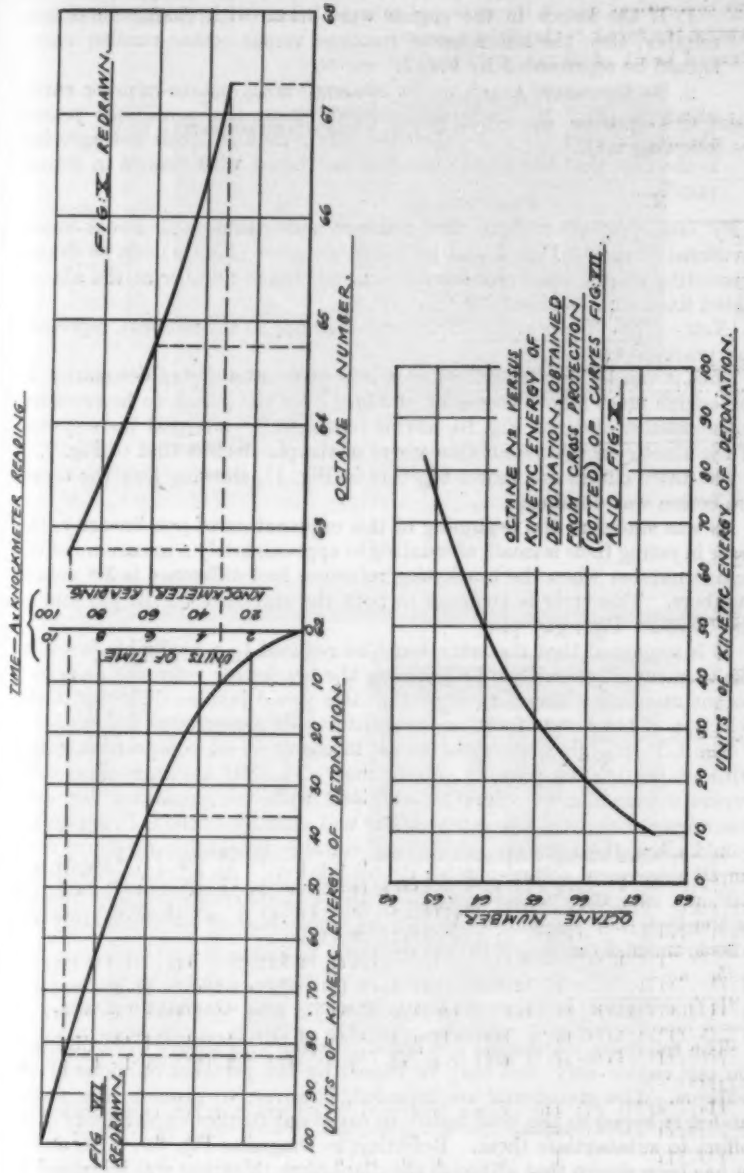


FIG. X REDRAWN
OCTANE NUMBER.
FIG. VII REDRAWN
UNITS OF KINETIC ENERGY OF DETONATION.
TIME—AX KNOCKMETER READING
KNOCKMETER READING
UNITS OF TIME
OCTANE NUMBER
OCTANE NO VERSUS KINETIC ENERGY OF DETONATION, OBTAINED FROM CROSS PROTECTION (DOTTED) OF CURVES FIG. VII AND FIG. X.
UNITS OF KINETIC ENERGY OF DETONATION.

Fig. 11.

Fig. 10 represents the result of two variables :—

1. If the knock in the engine were linear with change in octane number, then the knock-meter readings versus octane-number curve should be represented by Fig. 7.

2. As the *actual* knock-meter reading versus octane-number curve obtained (Fig. 10) does not coincide with the *previously proven* theoretical curve (Fig. 7), then the only reason for their not agreeing is the fact that the engine knock is not linear with change in octane number.

By cross-projection from the common side (time = A knock-meter divisions) of curves Figs. 7 and 10, a further curve (Fig. 11) can be drawn connecting kinetic energy of detonation and octane number at the above-stated fixed compression ratio.

(*Note.*—The " Units of Kinetic Energy " do not, at the moment, represent any practical value.)

Thus it can be seen that the knock impact or intensity of detonation in the engine must follow the curve of Fig. 11 for the knock to be recorded in the manner of curve, Fig. 10, having regard to the fact that the response of the kinetic energy versus time curve of the pin itself is that of Fig. 7.

The three curves are shown together in Fig. 11, showing how the cross-projection was obtained.

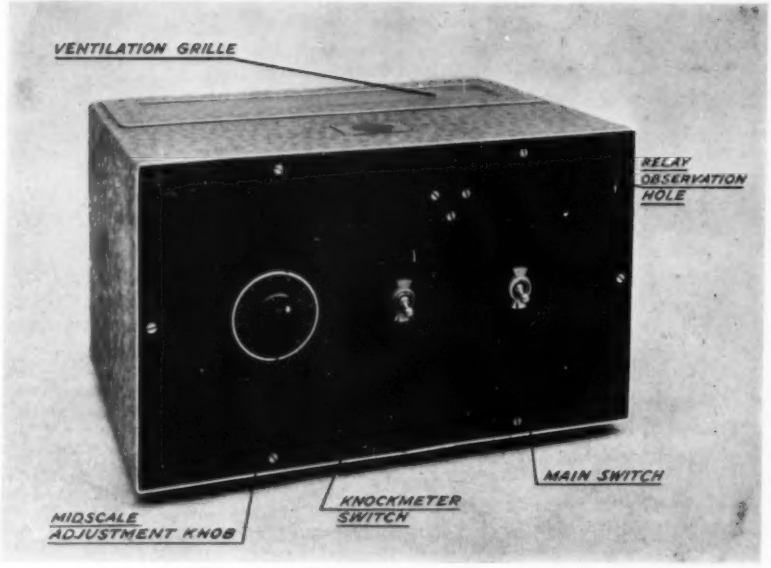
As was stated at the beginning of this explanation of non-linearity, the error in rating fuels is small, amounting to approximately a maximum of 0·2 octane number when the bracketing reference fuel difference is 3·8 octane numbers. This error is common to both the standard C.F.R. pin and to the Clement–Pigneguy pin.

It is suggested that the error could be reduced to a negligible factor in the Clement–Pigneguy pin by reducing the bracketing reference fuels to 2 octane numbers. Any suggestion that this would involve difficulty in the selection of bracketing fuels can be satisfactorily answered as follows :—

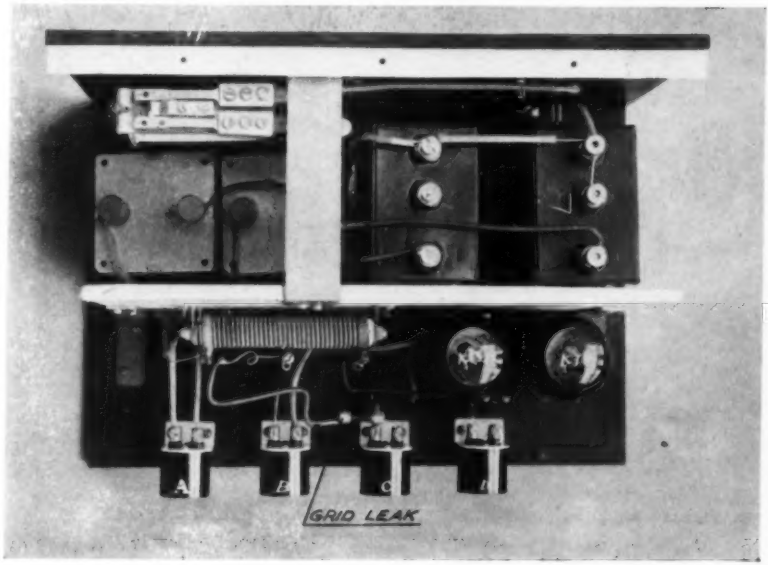
The C.P. pin gives standard knock intensity at all compression ratios without combustion-pressure interference. Thus, if a compression ratio versus octane-number curve be obtained with the apparatus for each test engine concerned, the repeatability and stability of the C.P. apparatus would allow the accurate selection of suitable bracketing reference fuels for all subsequent octane-number determinations. An advantage with the C.P. pin over the standard pin under the reduced octane-number bracket is the fact that the sensitivity can be maintained at approximately ten knock-meter divisions per octane number.

Discussion on Knock Measurement and Observed Data.

The following statements are based on data which have been obtained on one engine only, and may be biased by the personal opinions of the authors. The statements are included, however, to promote discussion, and it is hoped in the near future to carry out further experiments in an effort to substantiate them. Referring to Diagrams Fig. 6D, C, H, and G, it has been shown that although the diaphragm thickness was increased by 0·010 in., the energy of detonation transmitted through the diaphragm to



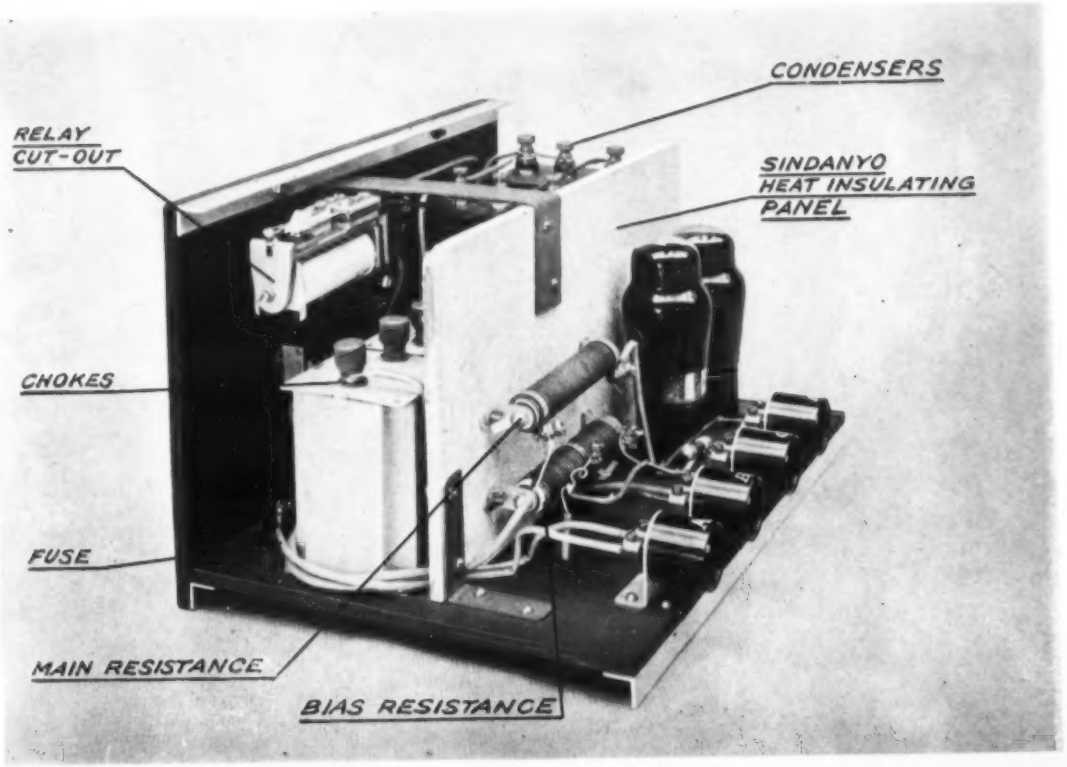
FRONT PANEL.



PLAN.

VIEWS OF "RADIO" SET.

[*To face p.* 508.



GENERAL INTERNAL VIEW OF "RADIO" SET.

the pin was not reduced. This gave rise to the suggestion that the thickness of the diaphragm could be increased without limit—*i.e.*, up to the thickness of the cylinder head. In other words, if a small mass is mounted externally on a solid part of the cylinder head, vibrations are set up in the mass due to the impact of detonation.

Accordingly a small apparatus was made up as follows :—

A $\frac{1}{8}$-in. diameter steel ball loaded with a coil spring was mounted in an insulated frame so that contact was only made by the ball on the cylinder head, which was polished to ensure a smooth contact surface. It was determined that this " pick-up unit " responded in an identical manner with the screwed-in pick-up unit.

An interesting use was made of this " bouncing-ball pick-up unit." As, of course, it is used externally, the bouncing-pin hole in the engine was available for use at the same time. Thus, using the standard C.F.R. pin and the bouncing-ball unit, together with two knock-meters, simultaneous readings on both systems were obtained and compared, and showed close agreement over the range where the standard pin was not recording combustion pressure—*i.e.*, at low compression ratios. This external pick-up shows the possibilities of the use of such an arrangement on engines not equipped for the fitting of screwed-in indicators, such as aircraft engines, etc.

The C.P. pin and the bouncing ball have both been tried out on a C.F.R. engine running under special high-speed conditions. During development of a method of test for rating high-octane fuels the units have shown that they each record detonation satisfactorily and respond to knock intensity described as " frequent slight." The engine speed during the tests was 1800 r.p.m., and jacket temperature using ethylene glycol was approximately 180° C., and the output was 120 B.M.E.P. One or two minor modifications may be necessary to the pick-up units—*e.g.*, greater rigidity and resistance to high temperatures—but, generally speaking, it can be stated that the system of measuring detonation is satisfactory at the high speed, and could be used for the rating of fuels.

At this point in the discussion it is considered appropriate to make reference to some experimental results which are of fundamental importance.

Up to the moment we have considered the effects of detonation on a mass situated on a diaphragm or in any case external to the engine, and have expressed its effects theoretically in " units of kinetic energy."

The following work was carried out on one engine, once only, and therefore the following theory put forward should be accepted with some reserve.

In an attempt to see what relation existed between knock-meter readings and the gas wave inside the cylinder, a " ball unit " referred to above was used simultaneouly with a normal cathode-ray oscillograph, the pick-up of which was screwed into the bouncing-pin hole. Then the engine was run at standard knock intensity on 65 O.N. fuel. At this engine setting both apparatus were set to record this knock intensity. In deference to accepted theory that detonation is high rate of change of pressure during the detonation wave, the oscillograph was set to record the rate of change of pressure diagram. The ball unit was adjusted to record a mid-scale reading on the knock-meter.

GENERAL INTERNAL VIEW OF " RADIO " SET.

With the apparatus thus set, the engine was run on fuels of various increasing octane numbers and the compression ratio correspondingly increased to give a mid-scale reading on the knock-meter recorded by the ball unit. At each individual reading so obtained it was noted that the height of the rate of change of pressure of detonation above that of normal combustion (*i.e.*, $Y_1 - Y$ in diagram, Fig. 12A) was constant. Thus it would appear that to measure the height of the rate-of-change diagram at the point of detonation would give a true indication of knock intensity.

In criticism of the Clement–Pigneguy principle, it has been stated that

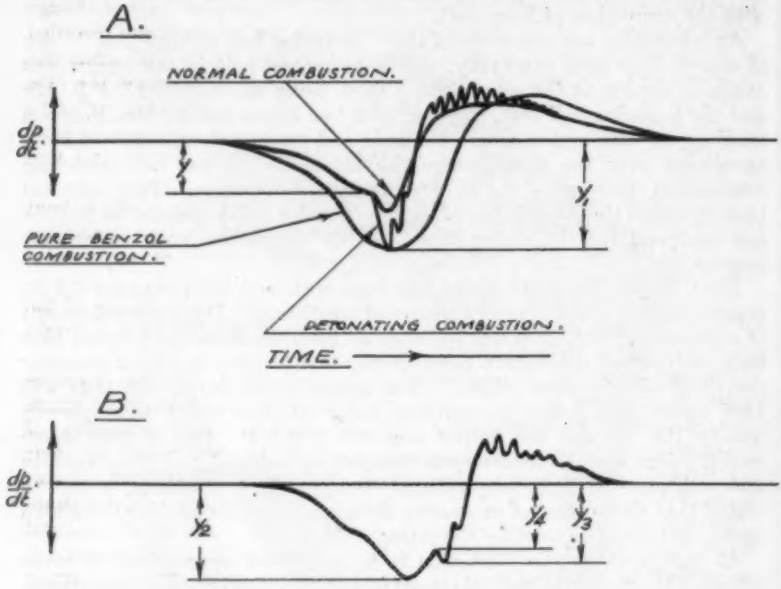


FIG. 12.

the mass of the pin is activated in its movement by the rate of change of pressure, and thus if the diagram of rate of change of pressure becomes similar to Fig. 12B by virtue of the nature of the fuel or the mixture strength used for the method of test, then the C.P. pin can no longer record detonation, but will respond to the maximum rate of change of pressure Y_2, and not to the detonation rate of change $Y_3 - Y_4$.

The following test results are intended to disprove any statement that the C.P. pin or the ball unit is activated by the rate of change of pressure, and an attempt is made to show that the principle of the apparatus is such that it is only activated by the second rate of change of pressure—*i.e.*, the rate of change of the rate of change of pressure. Furthermore, it is suggested that measuring the height of the rate-of-change diagram is only approximately what is required. That the method is reasonably satisfactory is because in general the height of the rate-of-change diagram is proportional to its *slope*.

Referring again to the simultaneous results obtained with the ball unit and the oscillograph, the following procedure was adopted.

The engine was run on a low-octane reference fuel and the compression ratio adjusted to give mid-scale reading on the knock-meter (standard knock intensity), and the height $Y_1 - Y$ of Fig. 12A noted.

Then the engine was switched over to pure benzol and the compression ratio increased considerably until the height of the rate-of-change-of-pressure diagram was equal to the peak value previously obtained on the low-octane fuel. (The two diagrams are drawn together, Fig. 12A.) At this setting of the compression ratio, and with the *maximum* rate of change of pressure exactly what it was on the detonating fuel, the ball unit recorded no knock-meter reading at all. Thus the evidence shows that while the maximum rate of change of pressure in both cases was the same, the rate of change of the rate of change of pressure was considerably different because of the comparatively smooth rise to maximum of the benzol curve; correspondingly the ball unit showed the difference as mid-scale and zero knock-meter readings, respectively.

Thus it may be claimed for the C.P. pin that it responds to the second differential of pressure d^2p/dt^2, and therefore smooth combustion no matter how rapid, will only be recorded as detonation when its d^2p/dt^2 approaches that of detonation.

Another criticism which has been made against the suggested use of the ball unit on high-output engines—*e.g.*, aircraft—is the fact that it would respond to engine vibration, valve-gear shock, etc.

Although no proof is available, it may be pointed out that the principle applied in the bouncing ball is much different from the principle on which other indicators are based. For instance, pick-up units consisting of electro-magnetic, electrostatic, or piezo-electric elements must, by their very nature, pick up engine vibrations which must be filtered out or compensated if their output is to be representative of intensity of detonation.

The ball unit or C.P. pin, being a mass loaded with a spring, is a natural "filter," and will only record the shock or impact of detonation when it has reached the intensity at which testing or investigation is to be carried out (which intensity is, of course, selected by the adjustment of the spring pressure). It is not expected, however, that the radio set output designed and satisfactory for the C.F.R. engine would be sufficient for direct application to any other engine. This output can easily be increased, however, by the addition of extra power-valves.

APPENDIX B.

The Performance of the Damping Circuit.

The conditions of this circuit are shown graphically in Fig. 13.

The shaded areas show the time of break of the negative bias circuit at the pin and diaphragm, for one detonation impact in the engine cylinder. A vibration is shown starting off long and gradually shortening, until after about thirteen individual breaks the pin comes to rest.

The curves represent quantities which have been calculated approxi-

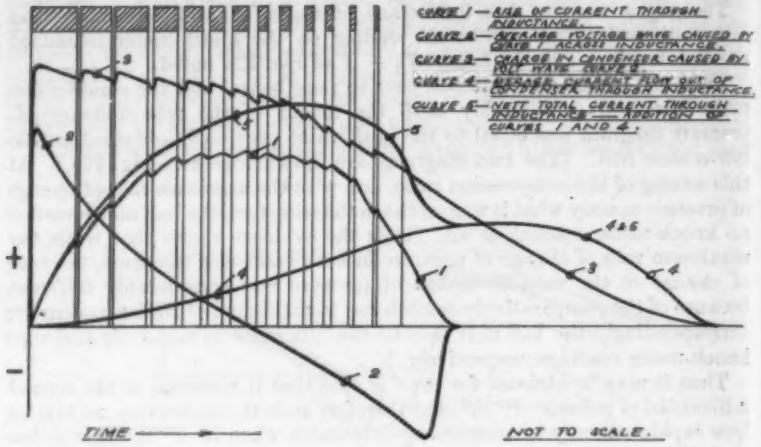
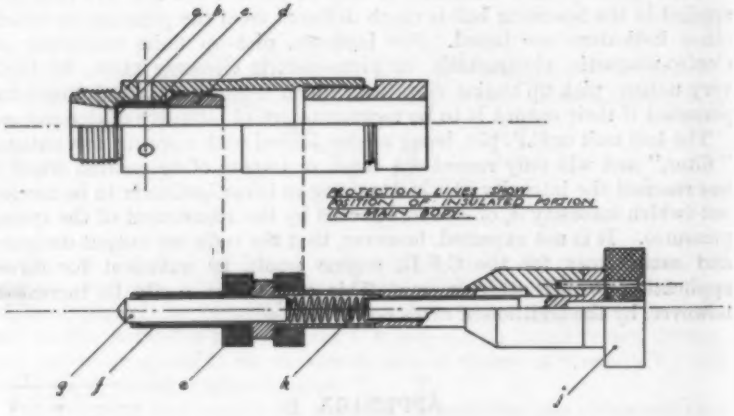

CURVE 1 — AMP. OF CURRENT THROUGH INDUCTANCE.
CURVE 2 — AVERAGE VOLTAGE WAVE CAUSED BY CURVE 1 ACROSS INDUCTANCE.
CURVE 3 — CHARGE IN CONDENSER CAUSED BY 1 OR 2 WAVE CURVE.
CURVE 4 — MEANER CURRENT FLOW OUT OF CONDENSER THROUGH INDUCTANCE.
CURVE 5 — NETT TOTAL CURRENT THROUGH INDUCTANCE = ADDITION OF CURVES 1 AND 4.
+
−
TIME
NOT TO SCALE.

FIG. 13.



C-A PICK-UP UNIT—MICROMETER HEAD TYPE.

FIG. 14.

mately from the constants of the circuit, and show the function for one condenser, one inductance, and resistance.

Curve 1 shows the rise of current through the inductance. The rate of change of Curve 1 is represented by Curve 2, and is thus the average voltage wave across the inductance. Now, by the known formula, Q, or quantity of electricity in Coulombs, is given by $Q = VC$, where $V =$ voltage across condenser of capacity C. Thus the condenser charges up from the voltage represented by Curve 2.

The discharge of the condenser through the inductance is limited in its rate by the D.C. resistance of the inductance. An approximate curve has been drawn in to illustrate the action. Curve 3.

The rate of change di/dt of Curve 1 given by Curve 2 falls to zero when Curve 1 reaches its maximum value, and thereafter reverses in sign.

This has the effect of gradually allowing the charge in the condenser to flow out through the inductance represented by Curve 4.

When, finally, the current represented in Curve 1 has fallen to zero, the charge shown in Curve 3 flows out through the inductance in a smooth manner after the knock impulse has finished (Curve 4). To arrive at the total current flowing through the inductance for one knock impulse shown, Curves 1 and 4 can be added together. They are shown so treated in Curve 5.

In the practical case Curve 5 would, of course, be parallel to the time base, showing a steady meter reading.

SYNTHESIS AND PROPERTIES OF MONO-NORMAL-ALKYLBENZENES.*

PART II.—PREPARATION AND PROPERTIES OF THE INTERMEDIATE KETONES AND CORRESPONDING HYDROCARBONS.

By T. Y. Ju, B.Sc., Stud.Inst.Pet., G. Shen, M.Sc., A.M.Inst.Pet., and C. E. Wood, M.Sc., A.I.C., F.Inst.Pet.

Synopsis.

A series of six mono-*n*-alkylbenzenes (alkyl group: C_5, C_6, C_7, C_9, C_{12}, C_{14}) has been prepared from the corresponding ketones by palladium catalytic hydrogenation and Clemmensen's reduction. The palladium catalytic hydrogenation method gives excellent yields and pure products. The ketones were obtained from the corresponding acid chlorides and benzene by Friedel and Crafts' reaction, the reaction medium being carbon disulphide. The yield of ketones decreases on ascent of the series. Optimum conditions for carrying out the hydrogenation and the Friedel and Crafts' reaction were studied. Certain physical properties of the ketone and hydrocarbon series have been determined and are compared with the values given in the literature. The experimentally determined linear relationships between density and temperature and refractive index and temperature are shown for both ketones and hydrocarbons. The effects of increasing chain length, in both instances, on the physical properties are systematically recorded. The phenyl group influences predominantly many of the physical properties of these *n*-alkylated benzenes even when the chain is long. For identification purposes three derivatives (semicarbazone, oxime, 2 : 4-dinitrophenylhydrazone) were prepared for each ketone, and the melting points of the derivations are given.

It is probable that these ketones and hydrocarbons have not been obtained in such large quantities previously. The amounts of ketones synthesized range from 800 to 1500 grams and the corresponding hydrocarbons from 400 to 450 grams. Every precaution has been taken to obtain both compounds in a state of purity, and this is borne out by referring the ketones and hydrocarbons to the criterion for purity of molecular refractivity and of course carbon and hydrogen determination.

From a review of the methods for the preparation of alkylbenzenes it was decided to reduce the *n*-alkyl phenyl ketones, and thus a series of *n*-alkylated benzenes ranging from *n*-amyl- to *n*-tetradecyl was prepared. The ketones were obtained by Friedel–Crafts' reaction from benzene and the corresponding acid chlorides, the reduction being effected by two methods :—

(1) Clemmensen's method.

(2) Catalytic hydrogenation in alcoholic solution in the presence of palladium deposited on animal charcoal.

Experimental.

Synthesis of Ketones.

(a) *Preparation and Preliminary Treatment of the Reagents.*

1. Acid chlorides.

(i) Caproic acid chloride, $CH_3(CH_2)_4COCl$, was redistilled and the fraction of boiling-point range 152–155° C./760 mm. was collected.

* Paper received 8th May, 1940.

(ii) Heptylic acid chloride, $CH_3(CH_2)_5COCl$, distilled *in vacuo*, had boiling point 65–66° C./15 mm.

(iii) Pelargonic acid chloride, $CH_3(CH_2)_7COCl$, distilled *in vacuo*, had boiling point 98–99° C./15 mm.

(iv) Lauric acid chloride, $CH_3(CH_2)_{10}COCl$, was prepared from lauric acid, $CH_3(CH_2)_{10}CO_2H$, of melting point 42–43° C. Fraction boiling between 134° and 137° C./11 mm. was used.

(v) Myristic acid chloride, $CH_3(CH_2)_{12}COCl$, prepared from myristic acid, $CH_3(CH_2)_{12}CO_2H$ of melting point 52–53° C. had boiling-point range 159–161° C./11 mm.

Method for the Preparation of the Last Two Acid Chlorides.—0·5 mole acid was put into a three-necked flask equipped with a mercury sealed stirrer, reflux condenser, and dropping funnel. The bath was heated until the acid was melted, 0·75 mole thionyl chloride (redistilled) was then introduced by means of a dropping funnel with gentle stirring. The flask was cooled by means of a water-bath to prevent too vigorous a reaction, but the temperature should be kept high enough to maintain the acid in liquid condition. Gentle suction was applied to the top of the condenser to remove the sulphur dioxide and hydrogen chloride evolved. The addition of thionyl chloride was finished in 1–1½ hours. After the thionyl chloride was added, the temperature of the bath was gradually raised to 60–65° C. in order to complete the reaction, and stirring was continued for a further 2 hours. The reaction product was then allowed to stand over-night and the acid chloride was purified by distilling twice *in vacuo*. Yield : 80–84 per cent. theoretical. Product, a colourless liquid.

2. Pure crystallizable benzene was dried over lime for several days and redistilled.

3. Carbon disulphide was dried over anhydrous calcium chloride.

4. Freshly prepared aluminium chloride was used.

(b) *Technique adopted for the Friedel–Crafts' Reaction.*

A 2-litre three-necked flask was fitted with a mercury sealed stirrer, condenser, and 500-c.c. dropping funnel. The flask was immersed in an ice-bath, the temperature not being allowed to rise above 10° C. To 1000 c.c. of carbon disulphide and 2 moles of crushed aluminium chloride a solution of the acid chloride (1·5 moles) in benzene (2·0 moles) was added drop by drop over a period of 1–1½ hours by means of the dropping funnel carrying a calcium chloride drying tube. The reacting mixture gradually darkens with evolution of hydrogen chloride, and suction was applied from the top of the condenser for its removal. Stirring is continued until hydrogen chloride ceased to be evolved. In most cases 30 hours were required. After completion of reaction the mixture is a homogeneous liquid with no solid aluminium chloride. The solution was poured slowly and without stirring into an equal volume of ice-water acidified with hydrochloric acid. The co-ordinated aluminium chloride compound hydrolyses slowly in the course of 1–2 hours. Stirring should be avoided, otherwise the temperature rises with rapid boiling of carbon disulphide and darkening of the product with formation of impurities. The carbon disulphide and aqueous layers were then separated by decantation from aluminium hydroxide, the former being steam distilled to

recover the carbon disulphide. Before distillation it is necessary to add 10 c.c. of concentrated hydrochloric acid to prevent foaming. When carbon disulphide ceases to come over the alkyl aryl ketone is left as an oily layer. Generally the crude product is brown and solidifies on cooling at room temperature. After purification the carbon disulphide is utilized in subsequent preparation.

Discussion.—The optimum ratios of carbon disulphide and aluminium chloride per mole of acyl chloride have been investigated.

Should a smaller quantity of carbon disulphide be used in the above Friedel–Crafts' reaction, the co-ordinated compound hydrolyses too energetically even on pouring very slowly onto ice, with resulting formation of a dark-coloured product. The use of a greater quantity of carbon disulphide does not improve the colour of the ketone to any great extent; further, the loss of carbon disulphide during suction and distillation is also increased.

As indicated in the previous paper, molecular quantities of aluminium chloride and the acyl chloride should be used for the acylation of benzene. In practice 1·3 mols. of aluminium chloride were required—*i.e.*, the reaction is catalysed; should a greater quantity be used, the excess does not dissolve in the carbon disulphide and causes trouble in hydrolysis.

(a) *Purification of Alkyl Aryl Ketones.*—The unreacted acyl chloride in the reaction mixture is hydrolysed ultimately to free acid which contaminates the ketone; for removal, the crude ketone is treated with boiling sodium carbonate solution (10 per cent.) and the soap separated. Finally the ketone is washed several times with hot water. In the case of higher fatty acids, as pelargonic, lauric, and myristic acids, the soaps are comparatively difficult to dissolve in water and readily emulsify the ketone. The most suitable method of purification is to add to the emulsified ketone anhydrous calcium chloride with stirring and allow the mixture to stand in a warm place. The calcium chloride dehydrates and carries down the soap as a sediment. The ketone can then be separated by decantation.

(b) *Separation of Resinous and Colouring Substances from the Crude Ketone.*—Attempts were made to purify the crude ketone by crystallization from the usual solvents (alcohol, benzene, petroleum ether, etc.). The product thus obtained showed little improvement with regard to colour and melting point. This may be due to adsorption of a resinous substance by the precipitating crystals. This resinous substance is possibly a neutral sulphur compound formed by interaction between carbon disulphide and benzene in the presence of aluminium chloride. (Heinrich Jörg, *Ber.*, 1927, 60*B*, 1466.)

(c) *Purification by Distillation in Vacuo.*—The distillates are generally colourless, but in the case of *n*-octyl, *n*-undecyl, and *n*-tridecyl phenyl ketones the distillates are faintly coloured pink. The ketone can be obtained white on repeated crystallization from alcohol. Generally a 5 per cent. black resinous residuum remained in the distilling flask which residue contains sulphur. Freshly distilled ketones have an objectionable odour which can be removed by washing with dilute sodium hydroxide solution. To obtain the ketones in a pure state, recrystallization three or even four times from alcohol is necessary.

Yield of Pure Ketones Based on the Weight of Acid Chlorides employed.

Ketones.	% Theoretical.
n-Amyl phenyl ketone	80
n-Hexyl phenyl ketone	86
n-Octyl phenyl ketone	78
n-Undecyl phenyl ketone	71
n-Tridecyl phenyl ketone	69

n-Butyl phenyl ketone was purchased and purified by vacuum distillation.

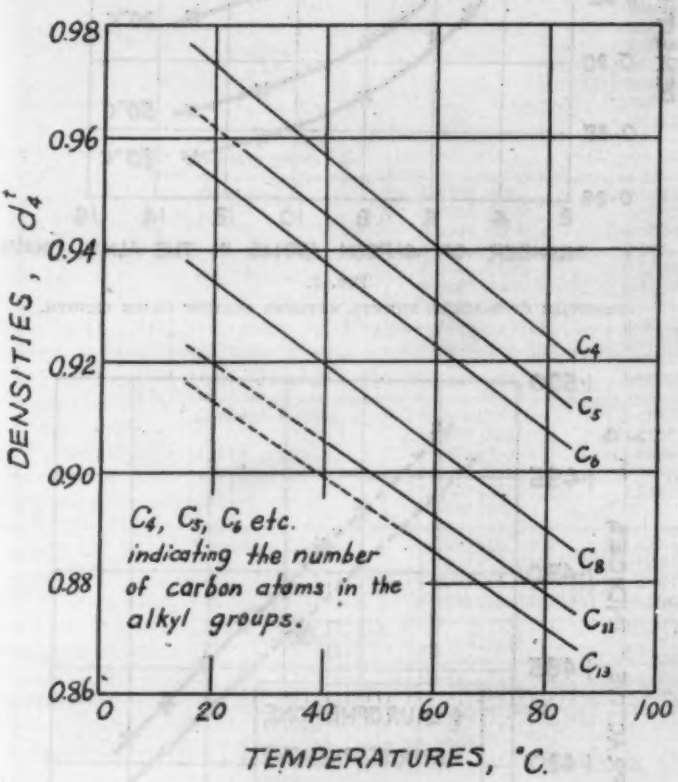


FIG. 1.

DENSITIES OF *n*-ALKYL PHENYL KETONES AGAINST TEMPERATURES.

Physical Properties of n-*Alkyl Phenyl Ketones.*

These are summarized in Table I.

A graph of the densities of the six ketones against temperatures is given in Fig. 1, the relationship being linear. The following data were interpolated or extrapolated.

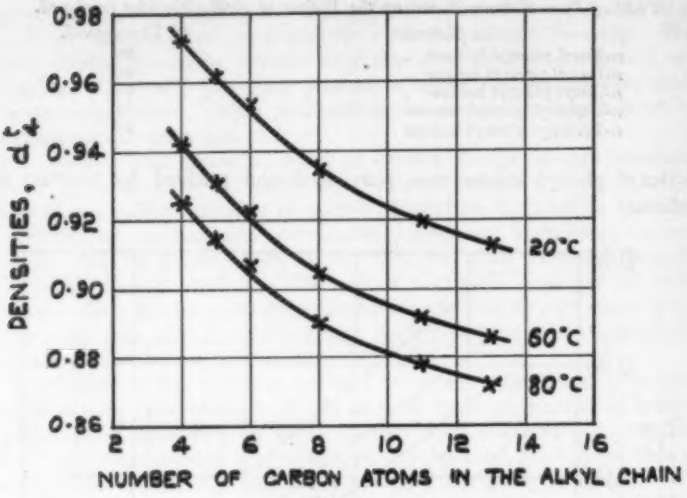


FIG. 2.

DENSITIES OF *n*-ALKYL PHENYL KETONES AGAINST CHAIN LENGTH.

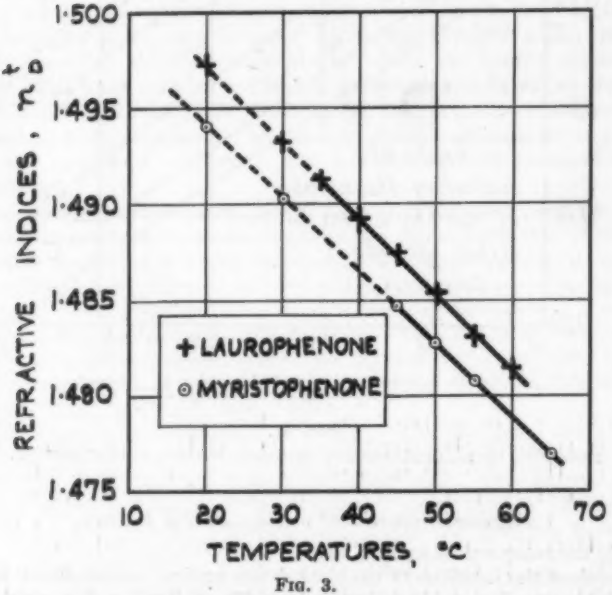


FIG. 3.

REFRACTIVE INDICES OF LAUROPHENONE AND MYRISTOPHENONE AGAINST TEMPERATURES.

		n-
CH
		Deter
va
Boiling point, ° C. (mm.)		116
Melting point, ° C.		
Densities, d_4^t		0·973
0·964
0·956
0·956
0·947
0·940
0·939
0·923
Refractive indices, n_D^t		1·514
1·510
Crystalline form		Li
Colour		Yell
Semicarbazone	Melting point, ° C.	1
	Colour	W
	Form	Ne
Oxime	Melting point, ° C.	
	Colour	W
	Form	Ne
2 : 4-Dinitrophenylhydrazone	Melting point, ° C.	1
	Colour	O
	Form	S
ne

[1] Beilstein, 1925, VII, 328.
[2] Auger, *Bull. de la Soc. Chim. de* stein, 1925, VII, 337).
[3] Layraud, *Bull. de la Soc. Chim.* (cf. Beilstein, 1925, VII, 328).
[4] Perkin and Calman, *J. chem. Soc* stein, 1925, VII, 328).
[5] Krafft, *Ber.*, 1886, **19**, 2987.
[6] Kipping and Russel, *J. chem.* Heilbron, "Dictionary of O 501).

		n-Butyl phenyl ketone, $CH_3(CH_2)_3CH_2CO,C_6H_5$.		n-A $CH_3($
		Determined value.	Values in literature.	Determ valu
Boiling point, ° C. (mm.)		116 (10)	248·5 [1] 144·5 (35) [2] 236–238 (720) [4] 242 [13] 131–133 (13) [15] 135–140 (25) [17]	111·5
Melting point, ° C.		−9		27
Densities, d_4^t		0·9731 (19·8) 0·9645 (30·1) 0·9566 (39·5) 0·9561 (40·6) 0·9479 (50·7) 0·9407 (59·7) 0·9393 (61·7) 0·9234 (81·0)	0·988 (d_{25}^{25}) [17]	0·9567 0·9527 0·9467 0·9450 0·9380 0·9308 0·9288 0·9148
Refractive indices, n_D^t		1·5148 (20) 1·5109 (30)	1·5152 (19) [2] 1·532 (20) [17]	1·5097 1·5050
Crystalline form		Liquid		Leafl
Colour		Yellowish		Yellow whit
Semicarbazone	Melting point, ° C.	166	166 [2, 15] 157–157·5 [17]	132
	Colour	White		Whit
	Form	Needles	Needles [2]	Needl
Oxime	Melting point, ° C.	55	52–52·5 [2] 51–52 [13] 52 [15]	52·5
	Colour	White		Whit
	Form	Needles	Needles [5, 13]	Needl
2 : 4-Dinitrophenylhydrazone	Melting point, ° C.	163·5		166
	Colour	Orange		Oran
	Form	Short needles		Fine needl

[1] Beilstein, 1925, VII, 328.
[2] Auger, *Bull. de la Soc. Chim. de France*, 1887, **47** (2), 50 (cf. Beilstein, 1925, VII, 337).
[3] Layraud, *Bull. de la Soc. Chim. de France*, 1906, **35** (3), 224–227 (cf. Beilstein, 1925, VII, 328).
[4] Perkin and Calman, *J. chem. Soc.* (*Lond.*), 1886, **49**, 161 (cf. Beilstein, 1925, VII, 328).
[5] Krafft, *Ber.*, 1886, **19**, 2987.
[6] Kipping and Russel, *J. chem. Soc.* (*Lond.*), 1895, **67**, 508 (cf. Heilbron, "Dictionary of Organic Compounds," 1936, II, 501).

TABLE I.

	n-Amyl phenyl ketone, $CH_3(CH_2)_3CH_2CO,C_6H_5$.		*n*-Hexyl phenyl ketone, $CH_3(CH_2)_4CH_2CO,C_6H_5$.		*n*-Octyl phenyl ketone, $CH_3(CH_2)_6CH_2CO,C_6H_5$.		*n*-Undecyl $CH_3(CH_2)$
	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.
	111·5 (4)	132–134 (14) [8] 258–260 [14] 265·2 [15] 145–150 (19) [17] 122–124 (15) [18]	141 (9)	267 (740) [2] 155 (15) [5] 277 [10] 160 (30) [10] 273–275 [14]	166 (9)	298–300 [14]	193–194 (9)
	27	27 [5, 14] 24·7 [15]	17	17 [2]	14	46 [14]	44–45
	0·9567 (26·8) 0·9527 (31·7) 0·9467 (39·5) 0·9450 (41·5) 0·9380 (50·3) 0·9308 (59·7) 0·9288 (61·9) 0·9148 (80·1)	0·95761 (25) [15] 0·95306 (30) [15] 0·981 (d_{25}^{25}) [17] 0·959 (18) [18]	0·9517 (21·2) 0·9393 (38·5) 0·9231 (59·7) 0·9076 (80·0)		0·9338 (20·5) 0·9328 (21·6) 0·9263 (30·2) 0·9197 (39·5) 0·9191 (40·0) 0·9109 (51·2) 0·9025 (62·4) 0·8890 (80·4)		0·9045 (41·5) 0·9012 (46·5) 0·8970 (53·0) 0·8933 (59·0) 0·8872 (66·8) 0·8848 (70·5) 0·8827 (73·0) 0·8762 (83·5)
	1·5097 (20) 1·5050 (30)	1·538 (20) [17] 1·516 (18) [18] 1·5178 (13·1) [18]	1·5081 (20) 1·5037 (30·1)	1·505 (?) [10]	1·5019 (20) 1·4977 (29·8)		1·4910 (35) 1·4890 (40) 1·4870 (45) 1·4851 (50) 1·4831 (55) 1·4812 (60)
	Leaflets	Leaflets [8]	Flakes		Flakes	Crystalline [14]	Flakes
	Yellowish-white		White		White		White
	132	132 [5, 14] 127–128 [17]	119	118–119 [10]	133·5	115 [14]	98
	White		White		White		White
	Needles	Needles [8]	Needles	Needles [10]	Needles		Needles
	52·5		54·5	55 [2]	53·5		64·5
	White		White		White		White
	Needles		Needles		Short needles		Short needles
	166		135	127–128 [10]	119·5		101–102
	Orange		Orange		Orange		Yellowish-orange
	Fine needles		Flakes		Flakes		Powder

[7] Eijkman, *Chem. Zentr.*, 1904, I, 1259 (cf. Heilbron, "Dictionary of Organic Compounds," 1936, II, 501).
[8] G. Schroeter, *Ber.*, 1907, **40**, 1589–1604 (cf. *C.A.*, 1907, **1**, 1989).
[9] A. Haller and E. Bauer, *Compt. rend.*, 1909, **149**, 5–10 (cf. *C.A.*, 1909, **3**, 2676).
[10] Colacicchi, *Atti della Reale Accad. dei Lincei* (*Rendiconti*), 1910, **19** (5), II, 503 (cf. Beilstein, 1931, VII, 180).
[11] von Auwers, *Ber.*, 1912, **45**, 2772 (cf. Beilstein, 1931, VII, 186).
[12] Mailhe, *Compt. rend.*, 1913, **157**, 220 (cf. Beilstein, 1931, VII, 173).
[13] Haller and Bauer, *Ann. de Chim. et de Phys.*, 1913, **28** (8), 410 (cf. Beilstein, 1931, VII, 173).
[14] P. Sabatier and
C.A., 1914,
[15] M. Tiffeneau a
C.A., 1927,
[16] I. Simon, *Bull.*
23, 4440).
[17] R. L. Shriner
1267–1269 (
[18] R. Truchet, *An*
[19] I. G. Farbenin
C.A., 1937,

TABLE I.

Hexyl phenyl ketone, $CH_3(CH_2)_4CH_2CO.C_6H_5$.		n-Octyl phenyl ketone, $CH_3(CH_2)_6CH_2CO.C_6H_5$.		n-Unde $CH_3(C$
rmined lue.	Values in literature.	Determined value.	Values in literature.	Determine value.
1 (9)	267 (740) [3] 155 (15) [5] 277 [10] 160 (30) [12] 273–275 [14]	166 (9)	298–300 [14]	193–194 (
17	17 [3]	14	46 [14]	44–45
" (21·2) 3 (38·5) 1 (59·7) 6 (80·0)		0·9338 (20·5) 0·9328 (21·6) 0·9263 (30·2) 0·9197 (39·5) 0·9191 (40·0) 0·9109 (51·2) 0·9025 (62·4) 0·8890 (80·4)		0·9045 (41· 0·9012 (46· 0·8970 (53· 0·8933 (59· 0·8872 (66· 0·8848 (70· 0·8827 (73· 0·8762 (83·
1 (20) 7 (30·1)	1·505 (?) [10]	1·5019 (20) 1·4977 (29·8)		1·4910 (35) 1·4890 (40) 1·4870 (45) 1·4851 (50) 1·4831 (55) 1·4812 (60)
lakes		Flakes	Crystalline [14]	Flakes
hite		White		White
119	118–119 [10]	133·5	115 [14]	98
hite		White		White
edles	Needles [10]	Needles		Needles
54·5	55 [3]	53·5		64·5
hite		White		White
edles		Short needles		Short needles
135	127–128 [10]	119·5		101–102
range		Orange		Yellowish-orange
lakes		Flakes		Powder

tr., 1904, I, 1259 (cf. Heilbron, "Dictionary ounds," 1936, II, 501).
907, **40**, 1589–1604 (cf. *C.A.*, 1907, **1**, 1989).
auer, *Compt. rend.*, 1909, **149**, 5–10 (cf. *C.A.*,
Reale Accad. dei Lincei (*Rendiconti*), 1910,
Beilstein, 1931, VII, 180).
912, **45**, 2772 (cf. Beilstein, 1931, VII, 186).
1913, **157**, 220 (cf. Beilstein, 1931, VII, 173).
nn. de Chim. et de Phys., 1913, **28** (8), 410
, VII, 173).

[14] P. Sabatier
C.A., 191
[15] M. Tiffeneau
C.A., 192
[16] I. Simon, *B*
23, 4440).
[17] R. L. Shrin
1267–1269
[18] R. Truchet,
[19] I. G. Farbe
C.A., 193

	n-Undecyl phenyl ketone, $CH_3(CH_2)_9CH_2CO,C_6H_5$.		*n*-Tridecyl phenyl ketone, $CH_3(CH_2)_{11}CH_2CO,C_6H_5$.	
	Determined value.	Values in literature.	Determined value.	Values in literature.
	193–194 (9)	201–202 (9) [9] 222–223 (21) [11] 174 (3) [10]	194–196 (4)	
	44–45	47 [8, 14] 45 [9] 46 [11]	52–53	55·5 [14]
	0·9045 (41·5) 0·9012 (46·5) 0·8970 (53·0) 0·8933 (59·0) 0·8872 (66·8) 0·8848 (70·5) 0·8827 (73·0) 0·8762 (83·5)	0·87935 (78·5) [7] 0·8969 (52·2) [11]	0·9886 (55·0) 0·8848 (60·2) 0·8811 (66·2) 0·8765 (72·5) 0·8708 (81·2)	
	1·4910 (35) 1·4890 (40) 1·4870 (45) 1·4851 (50) 1·4831 (55) 1·4812 (60)	1·47001 (n_a78·5) [7] 1·4850 (52·4) [11] 1·4815 (n_a52·4) [11] 1·4943 (n_β52·4) [11]	1·4848 (45) 1·4828 (50) 1·4809 (55) 1·4789 (60) 1·4769 (65)	
[14]	Flakes	Crystalline mass [8, 9]	Needles	Crystalline [14]
	White		White	
	98		101	75 [14]
	White		White	
	Needles		Flakes	Flakes [14]
	64·5		69·5	
	White		White	
	Short needles		Short needles	
	101–102		98–98·5	
	Yellowish-orange		Yellowish-orange	
	Powder		Powder	

[14] P. Sabatier and A. Mailhe, *Compt. rend.*, 1914, **158**, 830–835 (cf. *C.A.*, 1914, **8**, 2673).

[15] M. Tiffeneau and J. Levy, *Compt. rend.*, 1926, **183**, 969–971 (cf. *C.A.*, 1927, **21**, 908).

[16] I. Simon, *Bull. soc. Chim. Belg.*, 1929, **38**, 47–70 (cf. *C.A.*, 1929, **23**, 4440).

[17] R. L. Shriner and T. A. Turner, *J. Amer. chem. Soc.*, 1930, **52**, 1267–1269 (cf. *C.A.*, 1930, **24**, 1856).

[18] R. Truchet, *Ann. Chim.*, 1931, **16**, 309–419 (cf. *C.A.*, 1932, **26**, 2176).

[19] I. G. Farbenindustrie A.-G. Fr.P. 801,499, 5th Aug., 1936 (cf. *C.A.*, 1937, **31**, 483).

[*To face p.* 513.

	n-Amylbe $CH_3(CH_2)_9CH$
	Determined value.
Boiling point, ° C. (mm.)	77–78 (9) 204–205 (760)
Melting point, ° C.	
Densities, d_4^t	0·8702 (9·2) 0·8681 (11·5) 0·8541 (30·3) 0·8385 (49·8) 0·8384 (50·5) 0·8233 (69·8) 0·8039 (94·8)
Refractive index, n_D^t	1·4944 (14·8) 1·4920 (20) 1·4900 (25) 1·4878 (30) 1·4850 (35) 1·4830 (40)
Viscosity, ° C.	1·5780 C.S. (20) 1·0465 C.S. (50) 1·2260 C.S. (100° F.) 0·6605 C.S. (210° F.)
C.S.T. in aniline, ° C.	<-12

[1] Schramm, *Liebig's Ann. der Chem.*, 1883, **21**
[2] Auger, *Bull. de la Soc. Chim. de France*, 1
V, 452).
[3] Krafft, *Ber.*, 1886, **19**, 2987.
[4] J. V. Braun and H. Deutsch, *ibid.*, 1912,
2928).
[5] P. Sabatier and A. Mailhe, *Compt. rend.*, 1
8, 2673).
[6] L. G. Radcliffe and N. Simpkin, *J. Soc. c*
C.A., 1921, **15**, 3281).

TABLE IV.

n-Amylbenzene, $CH_3(CH_2)_3CH_2C_6H_5$.		n-Hexylbenzene, $CH_3(CH_2)_4CH_2C_6H_5$.		n-Heptylbenzene, $CH_3(CH_2)_5CH_2C_6H_5$.	
Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.
(9) 5 (760)	200·5–201·5 (743) [1] 200–201 (745) [4] 200·5–202 [6] 205·3 ± 0·1 [7] 198–202 [8] 81 (10) [10] 204–204·5 (750) [11] 205 [12] 87 (12) [16]	93–94 (9) 226–227 (760)	219–220 [4] 215 [5] 227·35 ± 0·1 [7] 97·5–101 (12) [16]	108–109 (9) 240–241 (760)	233 (760) [6] 110 (15) [9] 108–110 (10 235 [4] 240 [5] 116–118 (12
	−78·25 [7]		−66·8 [7]		
9·2) 11·5) 30·3) 49·8) 50·5) 69·8) 94·8)	0·8602 (22) [1] 0·8662 (20) [4] 0·8664 (*d*[15]) [6] 0·8651 (15·5) [6] 0·8624 (*d*[20]) [6] 0·8602 (22) [6] 0·87411 (0) [7] 0·86261 (15) [7] 0·85100 (30) [7] 0·8577 (20) [12] 0·8600 (20) [16]	0·8685 (9·0) 0·8526 (29·7) 0·8371 (49·8) 0·8223 (69·7) 0·8027 (94·8)	0·8613 (20) [4] 0·87527 (0) [7] 0·86394 (15) [7] 0·85259 (30) [7] 0·8592 (20) [16]	0·8678 (8·4) 0·8520 (29·7) 0·8370 (49·8) 0·8221 (69·7) 0·8039 (94·8)	0·8570 (20) 0·8590 (20)
14·8) 20) 25) 30) 35) 40)	1·4943 (20) [4] 1·4751 (15) [6] 1·4885 (20) [7] 1·4883 (20) [12] 1·4887 (20) [16]	1·4902 (20) 1·4881 (25) 1·4860 (30) 1·4811 (40)	1·490 (20) [4] 1·49132 (15) [7] 1·4868 (20) [16]	1·4902 (16·5) 1·4888 (20) 1·4868 (25) 1·4845 (30) 1·4822 (35) 1·4800 (40)	1·4865 (20) 1·4860 (20)
.S. (20) .S. (50) .S. (100° F.) .S. (210° F.)	1·487 C.P. (20) [7] 1·126 C.P. (30) [7] 1·547 C.S. (20) [16] 1·016 C.S. (50) [16]	2·0150 C.S. (20) 1·2770 C.S. (50) 1·4647 C.S. (100° F.) 0·7527 C.S. (210° F.)	1·833 C.P. (15) [7] 1·409 C.P. (30) [7] 1·91 C.S. (20) [16] 1·208 C.S. (50) [16]	2·4820 C.S. (20) 1·5160 C.S. (50) 1·7845 C.S. (100° F.) 0·8632 C.S. (210° F.)	2·39 C.S.(2 1·465 C.S.(5
−12	< −17 [9]	< −12	< −17 [9]	< −12	< −17 [9]

Chem., 1883, **218**, 388 (cf. Beilstein, 1922, V, 434).
n. de France, 1887, **47** (2), 48 (cf. Beilstein, 1922,

ibid., 1912, **45**, 2171–2188 (cf. *C.A.*, 1912, **6**,

Compt. rend., 1914, **158**, 830–835 (cf. *C.A.*, 1914,

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[9] Tilicheev and Kuryndin, *Neft Khoz.*, 1930, **1**
1931, **1**, 2560–2561).
[10] K. Ziegler, F. Dersch, and H. Wollthan, *Annal*
1934, **23**, 5430).
[11] F. Fichter and H. Stenzl, *Helv. chim. Acta*, 193
28, 6711).

TABLE IV.

	n-Heptylbenzene, $CH_3(CH_2)_5CH_2C_6H_5$.		*n*-Nonylbenzene, $CH_3(CH_2)_7CH_2C_6H_5$.		*n*-Dodecylbenzene, $CH_3(CH_2)_{10}CH_2C_6H_5$.	
	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.
	108–109 (9) 240–241 (760)	233 (760) [8] 110 (15) [8] 108–110 (10) [9] 235 [4] 240 [5] 116–118 (12) [16]	137·5–138·5 (9) 280–281 (760)	275 [5] 146 (14) [16]	172–173 (9)	138 (2) [13] 179–180 (13) 183–185 (12)
					−3	−7 [14]
	0·8678 (8·4) 0·8520 (29·7) 0·8370 (49·8) 0·8221 (69·7) 0·8039 (94·8)	0·8570 (20) [4] 0·8590 (20) [16]	0·8659 (9·2) 0·8513 (29·7) 0·8371 (49·8) 0·8226 (69·7) 0·8050 (94·8)	0·8616 (22) [9]	0·8636 (10·5) 0·8562 (21·1) 0·8496 (29·9) 0·8419 (40·6) 0·8356 (49·8) 0·8295 (59·0) 0·8225 (69·0) 0·8084 (89·8) 0·8013 (100·0)	0·8598 (d_4^{15}) [14] 0·8564 (20) [16]
	1·4902 (16·5) 1·4888 (20) 1·4868 (25) 1·4845 (30) 1·4822 (35) 1·4800 (40)	1·4865 (20) [4] 1·4860 (20) [16]	1·4863 (20) 1·4822 (30) 1·4781 (40)		1·4877 (13) 1·4847 (20) 1·4826 (25) 1·4806 (30) 1·4786 (35)	1·47431 (17) [14] 1·4822 (20) [16]
	2·4820 C.S. (20) 1·5160 C.S. (50) 1·7845 C.S. (100° F.) 0·8632 C.S. (210° F.)	2·39 C.S. (20) [16] 1·465 C.S. (50) [16]	3·7540 C.S. (20) 2·1105 C.S. (50) 2·4501 C.S. (100° F.) 1·1060 C.S. (210° F.)		6·5322 C.S. (20) 3·2674 C.S. (50) 4·2095 C.S. (100° F.) 1·5656 C.S. (210° F.)	4·864 C.P. (20) 3·575 C.P. (50) 6·294 C.S. (20) 3·197 C.S. (50)
	<−12	<−17 [9]	−12·3	−10·1 [9, 12]	13·7	15 [13]

...non, *Bull. Soc. chim. Belg.*, 1929, **38**, 47–70 (cf. *C.A.*, 1929, **23**, 4440).
...llman and J. Robinson, *Org. Syn.*, 1930, **10**, 4–5 (cf. *C.A.*, 1930, **24**, 1850).
...eev and Kuryndin, *Neft Khoz.*, 1930, **19**, 586–598 (cf. *Chem. Zentr.*, ...31, **1**, 2560–2561).
...egler, F. Dersch, and H. Wollthan, *Annalen*, 1934, **511**, 13–44 (cf. *C.A.*, ...4, **28**, 5430).
...hter and H. Stenzl, *Helv. chim. Acta*, 1934, **17**, 669–681 (cf. *C.A.*, 1934, ...6711).

[13] I. G. Farbenindustrie A.-G. Fr.P. 80... 483).
[14] V. N. Ipatieff and L. Schmerling, *J.* ... (cf. *C.A.*, 1938, **32**, 5795).
[15] A. D. Petrov and Leptova, *J. Gen.* ... 1938, **32**, 5386).
[16] Tilicheev, *Khim. Tverd. Topliva*, 193...
[17] A. W. Schmidt, G. Hopp, and V. S... *C.A.*, 1940, **34**, 730).

benzene, $CH_3.C_6H_5$.		n-Tetradecylbenzene, $CH_3(CH_2)_{12}CH_2.C_6H_5$.	
	Values in literature.	Determined value.	Values in literature.
	138 (2) [13] 179–180 (13) [14] 183–185 (12) [16]	195–196 (9)	153 (0·5) [16]
	−7 [14]	8·6	
	0·8598 (d_4^{15}) [14] 0·8564 (20) [16]	0·8629 (10·7) 0·8567 (20·0) 0·8500 (29·5) 0·8427 (39·5) 0·8359 (49·9) 0·8300 (59·7) 0·8223 (70·0) 0·8142 (82·4) 0·8078 (91·9) 0·8012 (101·9)	0·8559 (20) [16]
	1·47431 (17) [14] 1·4822 (20) [16]	1·4875 (12·3) 1·4844 (20) 1·4824 (25) 1·4805 (30) 1·4763 (40) 1·4724 (50)	1·4813 (20) [16]
	4·864 C.P. (20) [14] 3·575 C.P. (50) [14] 6·294 C.S. (20) [16] 3·197 C.S. (50) [16]	9·2302 C.S. (20) 4·2853 C.S. (50) 5·6099 C.S. (100° F.) 1·9584 C.S. (210° F.)	8·97 C.S. (20) [16] 4·26 C.S. (50) [16]
	15 [15]	27·3	29·0 [15]

A.-G. Fr.P. 801,499, 5th Aug., 1936 (cf. *C.A.*, 1937, **31**,

Schmerling, *J. Amer. chem. Soc.*, 1938, **60**, 1476–1479
5795).
ptova, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 207 (cf. *C.A.*,

rd. Topliva, 1938, **9** (2), 181–186.
Hopp, and V. Schoeller, *Ber.*, 1939, **72***B*, 1893–1897 (*cf.*

n-Dodecylbenzene, $CH_3(CH_2)_{10}CH_2.C_6H_5$.		n-Tetradecylbenzene, $CH_3(CH_2)_{12}CH_2.C_6H_5$.	
ined e.	Values in literature.	Determined value.	Values in literature.
	138 (2) [13] 179–180 (13) [14] 183–185 (12) [15]	195–196 (9)	153 (0·5) [16]
3	−7 [14]	8·6	
5) 1) 0) 9) 8) 0) 0) 7] ·0)	0·8598 (d_4^{15}) [14] 0·8564 (20) [15]	0·8629 (10·7) 0·8567 (20·0) 0·8500 (29·5) 0·8427 (39·5) 0·8359 (49·9) 0·8300 (59·7) 0·8223 (70·0) 0·8142 (82·4) 0·8078 (91·9) 0·8012 (101·9)	0·8559 (20) [16]
	1·47431 (17) [14] 1·4822 (20) [15]	1·4875 (12·3) 1·4844 (20) 1·4824 (25) 1·4805 (30) 1·4763 (40) 1·4724 (50)	1·4813 (20) [16]
(20) (50) (100° F.) (210° F.)	4·864 C.P. (20) [14] 3·575 C.P. (50) [14] 6·294 C.S. (20) [15] 3·197 C.S. (50) [15]	9·2302 C.S. (20) 4·2853 C.S. (50) 5·6099 C.S. (100° F.) 1·0584 C.S. (210° F.)	8·97 C.S. (20) [16] 4·26 C.S. (50) [16]
	15 [15]	27·3	29·0 [15]

nindustrie A.-G. Fr.P. 801,499, 5th Aug., 1936 (cf. *C.A.*, 1937, **31**,

leff and L. Schmerling, *J. Amer. chem. Soc.*, 1938, **60**, 1476–1479
, 1938, **32**, 5795).
ov and Lepteva, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 207 (cf. *C.A.*,
5386).
Khim. Tverd. Topliva, 1938, **9** (2), 181–186.
midt, G. Hopp, and V. Schoeller, *Ber.*, 1939, **72***B*, 1893–1897 (cf.
), **34**, 730).

TABLE II.

	C_6H_5CO,C_6H_5.	$C_9H_{11}CO,C_6H_5$.	$C_8H_{13}CO,C_6H_5$.	$C_9H_{17}CO,C_6H_5$.	$C_{11}H_{23}CO,C_6H_5$.	$C_{13}H_{27}CO,C_6H_5$.
20° C.	0·9728	0·9619	0·9526	0·9342	0·9196	0·9124
60° C.	0·9403	0·9306	0·9228	0·9042	0·8918	0·8852
80° C.	0·9241	0·9149	0·9077	0·8894	0·8781	0·8716

A further graph comparing the effects of the number of carbon atoms in the alkyl group on the densities of ketones at 20°, 60°, and 80° C. is given in Fig. 2. The convex curvature shows that, on ascent of the homologous alkyl phenyl ketones, the difference of density between successive higher members decreases for the temperatures investigated.

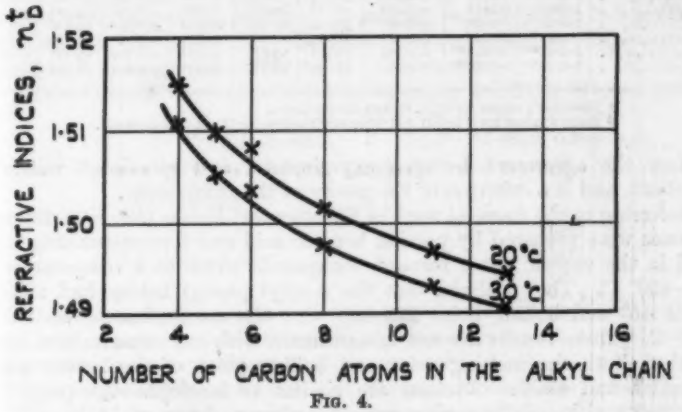


FIG. 4.

REFRACTIVE INDICES OF *n*-ALKYL PHENYL KETONES AGAINST CHAIN LENGTH.

The curves are roughly parallel, and there is no distinguishable differentiation between even and odd members in the chain length.

The variation of refractive indices with temperatures for laurophenone and myristophenone which is linear is shown in Fig. 3, from which the following data were extrapolated :—

	$C_{11}H_{23}CO,C_6H_5$.	$C_{13}H_{27}CO,C_6H_5$.
n_D^{20}	1·4970	1·4942
n_D^{30}	1·4931	1·4904

The effect of the number of carbon atoms in the alkyl chain on the refractive indices for the six ketones at 20° and 30° C. for D line is shown in Fig. 4. The curves are again convex towards the axis, and the difference of refractive index between homologues decreases on ascent of the series. It is to be noted that the refractive index for the hexyl (6) member does not lie on the curve; this difference (experimental value–interpolated value) lies outside the possible experimental error. This member also shows slight anomaly in relationship to other members with regard to its density.

It is interesting to compare the observed data for the molecular refractivity with calculated data using the Eisenlohr and Hulst values for atomic refractivities.

	Eisenlohr.	Hulst.
C	2·418	2·590
H	1·100	1·025
Double bond	1·733	—
Oxygen, ketonic	2·211	—

TABLE III.

	n_D^{20}.	d_4^{20}.	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	Mol. weight.	Mol. refract., obs.	Mol. refract., calc.[a]	Obs.–Calc.[a]	Mol. refract., calc.[b]	Obs.–Calc.[b]
C_6H_5CO,C_6H_5	1·5148	0·9728	0·30988	162·11	50·234	49·408	+0·836	50·250	−0·016
$C_6H_{11}CO,C_6H_5$	1·5097	0·9619	0·31078	176·12	54·734	54·026	+0·708	54·890	−0·156
$C_6H_{13}CO,C_6H_5$	1·5081	0·9526	0·31297	190·14	59·507	58·644	+0·863	59·530	−0·023
$C_8H_{17}CO,C_6H_5$	1·5019	0·9342	0·31585	218·17	68·908	67·880	+1·028	68·810	+0·098
$C_{11}H_{23}CO,C_6H_5$	1·4812[80°]	0·8918[80°]	0·31923	260·21	83·070	81·734	+1·336	82·730	+0·340
$C_{13}H_{27}CO,C_6H_5$	1·4789[40°]	0·8852[40°]	0·31902	288·25	92·327	90·970	+1·357	92·010	+0·317

[a] Eisenlohr's values for C, H, O, and double bonds.
[b] Hulst's values for C and H and Eisenlohr's values for O and double bonds.

Here the agreement between experimental and calculated values is excellent, and is a criterion of the purity of the compounds.

Referring to the classical work of Sabatier and Mailhe (*loc. cit.*), different ketones were prepared by passing benzoic acid and a corresponding fatty acid in the vapour phase through manganous oxide at a temperature of 400–450° C. They claimed that the *n*-octyl phenyl ketone had melting point 46° and boiling point 298–300° C.; the semicarbazone melted at 115° C. These results are not in agreement with our experimental facts, further, both the melting point and boiling point of the ketone which Sabatier and Mailhe obtained are similar to benzophenone (m.p. 48°, b.p. 305°), although benzophenone semicarbazone has m.p. 164°.

The carbon and hydrogen determinations are given below.

C_6H_5CO,C_6H_5	C, 81·50 (Theory 81·43) H, 8·69 (Theory 8·70)	$C_8H_{17}CO,C_6H_5$	C, 82·39 (Theory 82·51) H, 10·36 (Theory 10·16)
$C_6H_{11}CO,C_6H_5$	C, 81·61 (Theory 81·77) H, 9·32 (Theory 9·16)	$C_{11}H_{23}CO,C_6H_5$	C, 82·57 (Theory 83·01) H, 10·99 (Theory 10·84)
$C_6H_{13}CO,C_6H_5$	C, 81·98 (Theory 82·05) H, 9·76 (Theory 9·54)	$C_{13}H_{27}CO,C_6H_5$	C, 83·28 (Theory 83·26) H, 11·31 (Theory 11·19)

The authors are indebted to Mr. J. Khalili, B.Sc., for experimental work relating to the melting points, derivatives, and refractive indices of certain ketones and hydrocarbons.

Hydrogenation of Alkyl Aryl Ketones.

(1) *Reduction by Zinc Amalgam.*—Zinc foil cut into small strips was left for 1 hour with frequent shaking in contact with an equal weight of 5 per cent. aqueous mercuric chloride solution. The solution was then poured off and the zinc amalgam washed with fresh water.

Conical flasks fitted with ground joint reflux condensers were used. To the mixture of 100 c.c. concentrated hydrochloric acid 200 c.c. water and 150 grams of zinc amalgam; half mole of alkyl aryl ketone was

added, and the whole boiled vigorously; 50 c.c. concentrate hydrochloric acid were added hourly until a total of 400 c.c. acid had been employed. Hydrogen is evolved only at the boiling point, and the reaction was allowed to proceed until the zinc was practically dissolved. The oily layer was separated, washed several times with hot water, dried over calcium chloride, and distilled *in vacuo*. Generally, yields of 65–75 per cent. of hydrocarbons, boiling within a range of 6° C., were obtained. The residues obtained on distillation were of high boiling point and of high viscosity. The oils partly crystallized on keeping. The constitution of these oily residua has not been investigated; they are probably pinacones the formation of which is favoured by this method of reduction.

The hydrocarbon was purified by heating for some hours with freshly cut sodium at 160° C. (approx.), then cooled and distilled *in vacuo* in contact with the molten sodium. A gummy residue (about 2–3 per cent.) remained in the flask. The distillate was redistilled *in vacuo* and the fraction, b.p. range not exceeding 1° C., collected.

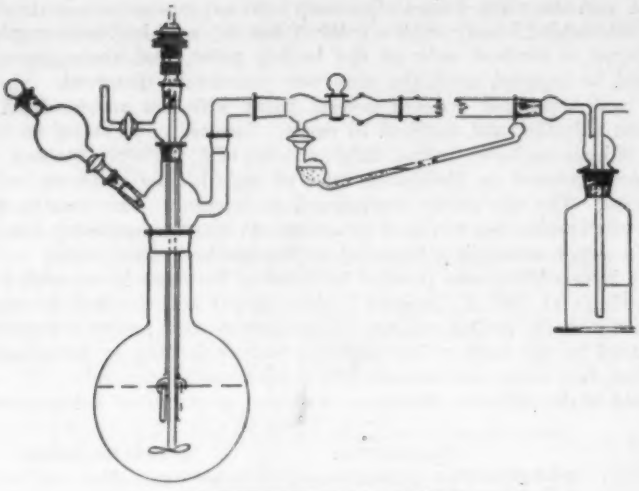
Yield of the different alkylbenzenes based on weight of ketones used :—

Hydrocarbons.	% Yield theoretical.
n-Amylbenzene	58
n-Hexylbenzene	56
n-Heptylbenzene	53
n-Nonylbenzene	51
n-Dodecylbenzene	41
n-Tetradecylbenzene	39

For efficient hydrogenation the ketone should be pure and sulphur free, and repeated distillations *in vacuo* and repeated crystallizations (frequently four recrystallizations) are necessary.

(2) *Catalytic Hydrogenation.*—The ketones in alcoholic solution were hydrogenated to corresponding alkylbenzenes under a pressure slightly above atmospheric in the presence of palladium deposited on animal charcoal. A stationary apparatus was designed for this purpose. All connections were fitted with ground joints, and rubber tubing was used only to connect the hydrogen cylinder to the safety device and the apparatus.

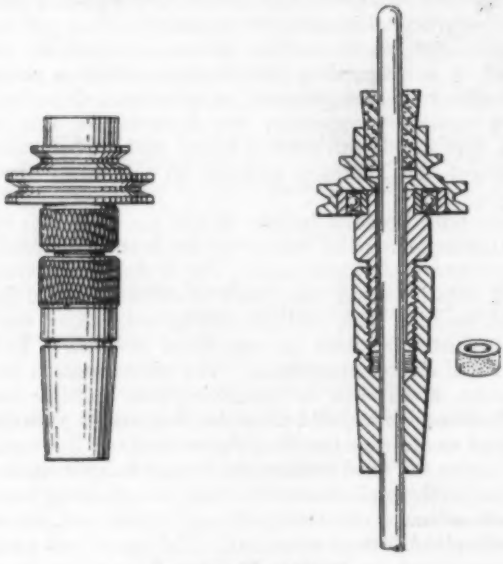
There were four Drechsel bottles of 125 c.c. capacity, of which two contained alkaline pyrogallol (nearer to the hydrogen cylinder), and the other two, concentrated caustic soda. The drying tube contained calcium chloride and soda lime and was $\frac{3}{4}$-inch in diameter and 2 feet in length. Between the reaction flask and the drying tube there was an inclined mercury manometer in which the maximum pressure of hydrogen could be read to 7 cm. above atmospheric. The hydrogenation flask was 1- or 2-litre capacity, fitted with an interchangeable multiple adapter, dropping funnel, stirrer sleeve, and a special link stirrer with gland fittings. The stirrer had an ordinary paddle at the end and two link paddles attached at 3 inches above the fixed paddle, the former being used for distribution of the catalyst in the medium and the latter for the spraying of the liquid. The stirrer sleeve had a side-tube with a stop-cock, and was used as a gas outlet. Brass gland fittings were used. The gland was packed with felt washer or asbestos string lubricated with soft wax, and incorporated an



THE HYDROGENATION APPARATUS.

aluminium pulley mounted by means of a ball race. The stirrer was locked to the pulley by means of cork.

Animal charcoal obtained commercially may contain traces of metallic sulphide which render palladium inactive. To remove this impurity, the



THE STIRRER GLAND.

charcoal was boiled with dilute hydrochloric acid for a few minutes, filtered by suction, washed several times with hot water, and dried. Finally, it was heated strongly in a crucible to remove any volatile matter.

10 grams of purified animal charcoal were suspended in 350 c.c. of distilled water in the 1-litre hydrogenation flask. The stopcock in the side tube of the stirrer sleeve was opened and hydrogen was passed in order to displace all air in the apparatus. The stopcock was closed and the pressure of hydrogen allowed to rise to 7 cm. Hg, above which hydrogen will escape from the safety device adjacent to the cylinder. The stopcock of the drying tube was closed, the hydrogen supply cut off, and the manometer then indicated whether the pressure remained constant within the apparatus. Slight leaking through the stirrer gland was sometimes unavoidable. On release of the pressure, hydrogen was passed continuously, whilst a solution of 0·5 gm. palladium chloride in 100 c.c. of 0·1*N*-hydrochloric acid was gradually run into the flask from a dropping funnel. After closing the gas outlet stopcock, spraying was begun, and the hydrogen pressure adjusted to about 5 cm. Hg. Reduction began immediately. Subsequently the catalyst was filtered on a Buchner funnel, washed free from acid, then twice with alcohol and once with ether; it was transferred to a desiccator, which was evacuated and kept in the dry condition until ready for use.

For hydrogenation, 50 grams of pure ketone dissolved in 800 c.c. absolute alcohol were introduced into a 2-litre flask, together with 5 gm. of the palladium deposited charcoal (equivalent to 0·25 gm. $PdCl_2$). The procedure of hydrogenation was similar to that for preparing the catalyst, the time required for completion of hydrogenation being generally from 20 to 30 hours. The catalyst was removed and the filtrate distilled on a water-bath to recover the alcohol.

The residuum was distilled *in vacuo*, the hydrocarbon being subsequently purified with sodium and redistilled.

The recovered catalyst was not suited for further use in hydrogenation, for its activity was considerably decreased.

n-Hexyl-, *n*-heptyl-, *n*-nonyl-, and *n*-dodecyl-benzenes have been prepared by this method. Excellent yields and very pure products for the first three hydrocarbons have been obtained.

Many difficulties have been experienced in hydrogenating laurophenone. The above procedure failed and was modified. Hydrogen pressure of 7 cm. Hg was maintained throughout the hydrogenation instead of 5 cm. Hg employed in other cases. Half the amount of the catalyst was added in portions on subsequent days. Although the difficulties in carrying out the hydrogenation were overcome by these modifications, yet the yield was low.

Yield of purified hydrocarbons based on the weights of ketones used :—

Hydrocarbons.	% Yield theoretical.
n-Hexylbenzene	95
n-Heptylbenzene	93
n-Nonylbenzene	92
n-Dodecylbenzene	76

Traces of sulphur compounds present in the mixture stop the hydro-

genation completely. The ketones should be distilled *in vacuo* and recrystallized several times from alcohol (cf. Clemmensen's method) and tested for sulphur. No lubricant was used for glass joints and for gland fittings; a sulphur-free soft wax was used. To obtain efficient spraying, the level of the solution should be just below the top of the link paddles.

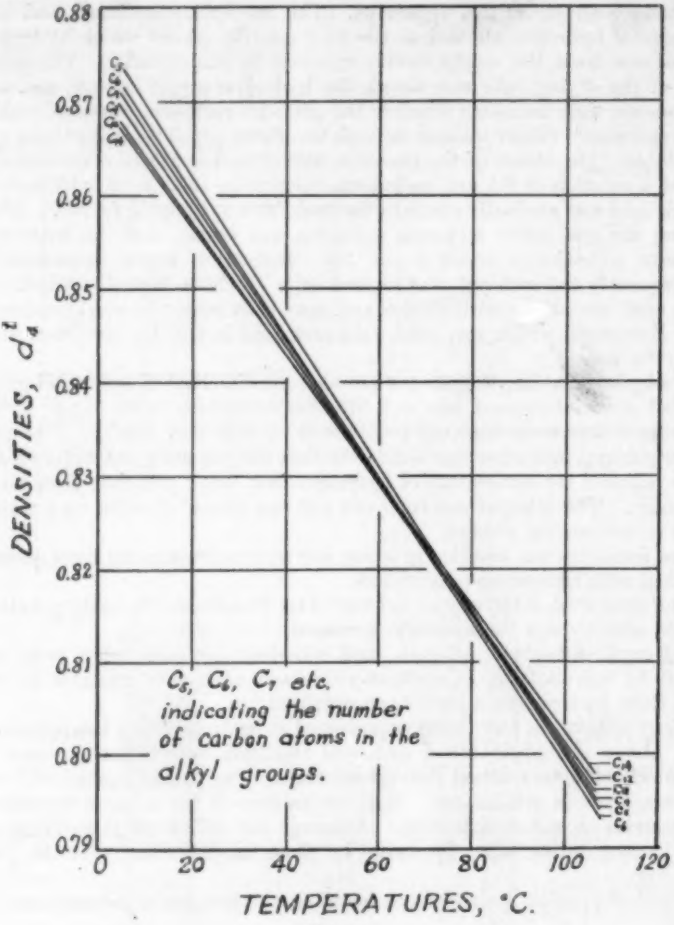


FIG. 5.

DENSITIES OF *n*-ALKYL BENZENES AGAINST TEMPERATURES.

Physical Properties of Hydrocarbons.

Various physical properties of the hydrocarbons so prepared have been determined, and are tabulated and compared with the values given in the literature (Table IV).

The densities of six *n*-alkylbenzenes plotted against temperatures is given in Fig. 5; change of density with temperature is linear of course. The following data were interpolated from this graph :—

TABLE V.

	$C_5H_{11}.C_6H_5$.	$C_6H_{13}.C_6H_5$.	$C_7H_{15}.C_6H_5$.	$C_8H_{17}.C_6H_5$.	$C_{12}H_{25}.C_6H_5$.	$C_{16}H_{33}.C_6H_5$.
10° C.	0·8695	0·8676	0·8666	0·8653	0·8638	0·8634
20° C.	0·8618	0·8600	0·8592	0·8582	0·8568	0·8566
70° C.	0·8230	0·8217	0·8222	0·8224	0·8220	0·8225
95° C.	0·8038	0·8025	0·8038	0·8044	0·8047	0·8056

These data are given in Fig. 6, which shows the effect of the number of

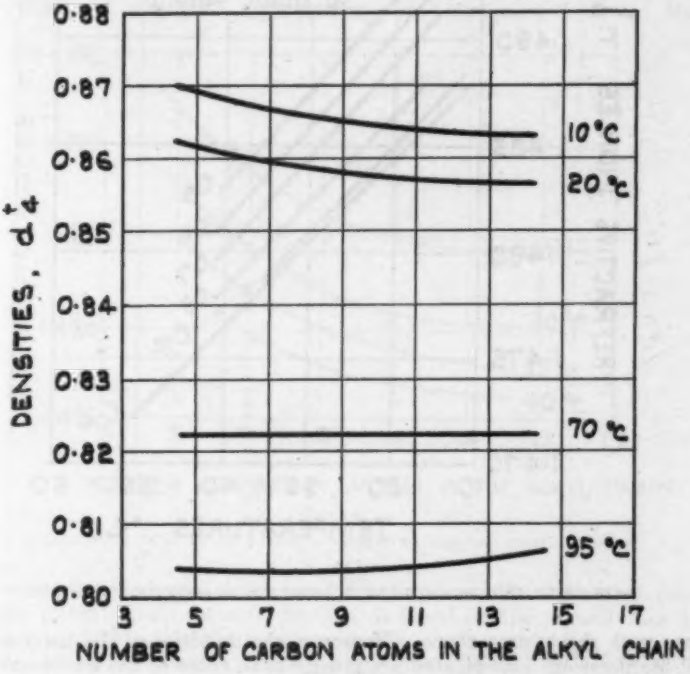


FIG. 6.

DENSITIES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

carbon atoms in the alkyl chain on the densities at the four temperatures. The longer the chain attached to the benzene nucleus the lower is the density at lower temperatures (below 50° C.). This effect diminishes with increase of the chain length. For higher temperatures (above 70° C.), however, increase of chain length causes very little change in density, and at 70° C. the six hydrocarbons have practically the same density.

At still higher temperatures (above 90° C.) increase of chain length, on the contrary, causes increase in density.

Comparison of Fig. 2 (ketones) and Fig. 6 (hydrocarbons) (cf. also Tables II and V) for densities and chain-length relationships shows how widely the two homologous series differ. Fig. 2 shows that density with increase of number of carbon atoms decreases rapidly, which is not the

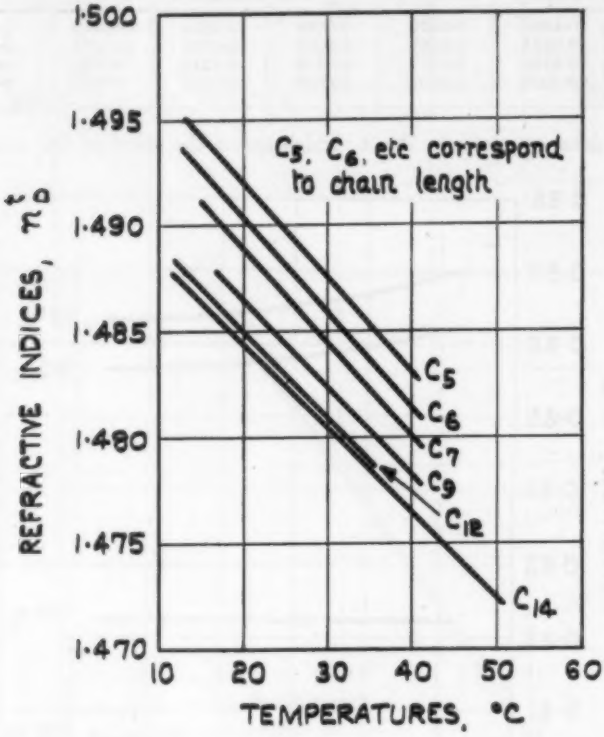


FIG. 7.

REFRACTIVE INDICES OF *n*-ALKYL BENZENES AGAINST TEMPERATURE.

case with the hydrocarbons. Moreover, the densities of the ketones for all temperatures investigated are greater than those of the hydrocarbons.

The variation of refractive indices at different temperatures is shown as Fig. 7, the relationship also being linear. The effect of the number of carbon atoms in the alkyl chain on the refractive index for D line at 20°, 30°, 35°, and 40° C. (given in Table IV) is plotted in Fig. 8. The decrease in refractive index caused by the increasing chain length diminishes on ascent of the series. The curves are practically parallel, and whatever stereochemical structure these alkylbenzenes possess there is no apparent differentiation into even and odd members. In Table VI the experi-

mentally determined and calculated values of the molecular refractivity are compared.

TABLE VI.

	$n_D^{20.}$	$d_4^{20.}$	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	Mol. weight.	Mol. refract., obs.	Mol. refract., calc.[a]	Obs.–Calc.[a]	Mol. refract., calc.[b]	Obs.–Calc.[b]
$C_5H_{11}.C_6H_5$ . .	1·4920	0·8618	0·33863	148·13	49·865	49·397	+0·468	50·089	−0·224
$C_6H_{13}.C_6H_5$ . .	1·4902	0·8600	0·33832	162·14	54·530	54·015	+0·515	54·729	−0·199
$C_7H_{15}.C_6H_5$ . .	1·4888	0·8592	0·33579	176·16	59·154	58·633	+0·521	59·369	−0·215
$C_8H_{17}.C_6H_5$ . .	1·4863	0·8582	0·33472	204·19	68·348	67·869	+0·479	68·649	−0·301
$C_{12}H_{25}.C_6H_5$ . .	1·4847	0·8568	0·33434	246·23	82·324	81·723	+0·601	82·569	−0·245
$C_{14}H_{29}.C_6H_5$ . .	1·4844	0·8566	0·33424	274·27	91·672	90·959	+0·713	91·849	−0·177

[a] Eisenlohr's values for C, H, and double bonds.
[b] Hulst's values for C and H and Eisenlohr's values for double bonds.

It is to be noted that all the values of *observed-a* are positive and all the values of *observed-b* are negative; in both cases, however, these

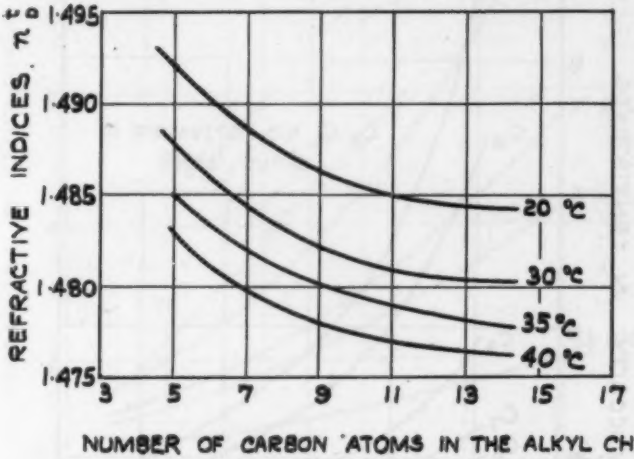


FIG. 8.

REFRACTIVE INDICES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

differences range about a mean but different value. The calculated value for the phenyl group (benzene nucleus) is based on the refractivities for 6C, 5H, and three double bonds, and also on the statement that ring closure affects the molecular refractivity but slightly. It would seem, from a consideration of the sign of the differences obtained, that a better value for the refractivity of the phenyl group could be obtained from an experimentally determined average value for this group—viz., from a large number of refractive indices of aromatic compounds. Still the differences are only a small percentage of the molecular refractivity in each case. The using of Hulst's values for carbon and hydrogen gives results in better agreement with the observed values. The Abbé Refractometer at constant temperatures was used in these determinations.

Kurtz and Ward (*J. Frank. Inst.*, 1936, **222**, 563) calculate the refractive intercept (the intercept on the ordinate axis of a plot of n_D^{20} against d_4^{20}) of the aromatics as 1·0627 and of the paraffins as 1·0461. They propose the refractive intercept, $b = n - \frac{d}{2}$. The values of b in the present investigation are :—

$C_5H_{11}C_6H_5$	1·0611	$C_9H_{19}C_6H_5$	1·0572
$C_6H_{13}C_6H_5$	1·0602	$C_{12}H_{25}C_6H_5$	1·0563
$C_7H_{15}C_6H_5$	1·0592	$C_{14}H_{29}C_6H_5$	1·0561

It is clear, with regard to this physical property, that the value regularly and consistently diminishes as would be expected, but the phenyl group

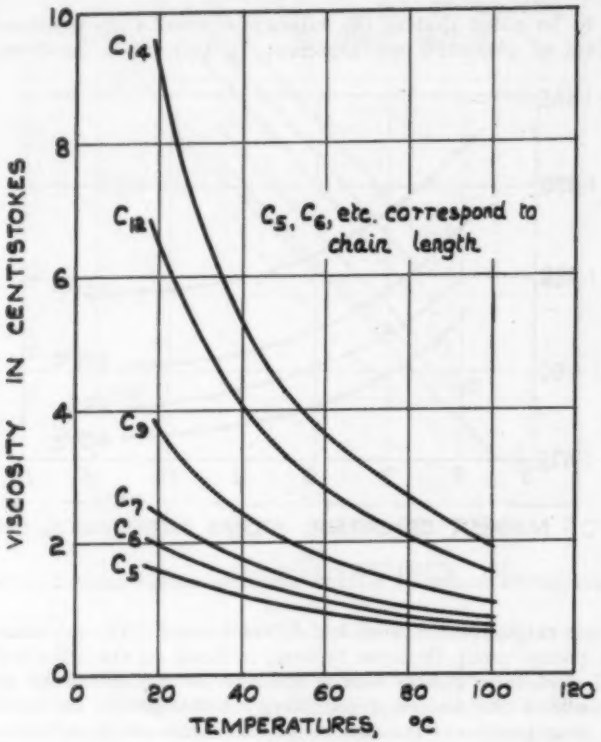


FIG. 9.

VISCOSITIES OF n-ALKYL BENZENES AGAINST TEMPERATURES.

predominantly influences the value even when the chain is long (C_{14}). The value never approaches that for paraffins.

Comparisons of Fig. 4 (ketones) and Fig. 8 (hydrocarbons) (cf. also Tables I and IV) shows the influence in the visible region of the absorption band of the carbonyl group in raising the refractive index, the molecular

refractivity being, as would be expected, almost identical for ketones and hydrocarbons (cf. Tables III and VI).

The viscosities in centistokes of the hydrocarbons plotted against temperatures are given in Table IV and Fig. 9. The diagram obtained is typical of a series of normal homologues—ascent of the series causing increase of viscosity. The coefficient of change of viscosity with temperature increases as the series is ascended. The graph indicates the viscosities of

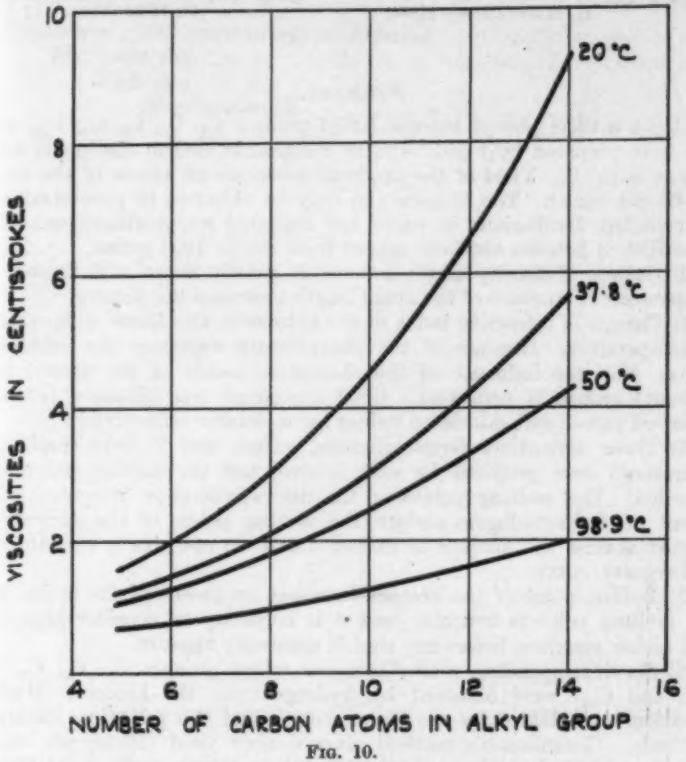


FIG. 10.

VISCOSITIES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

the alkylbenzenes of increasing chain length corresponding to carbon atoms 5, 6, 7, 9, 12, and 14, but it does not indicate viscosities of successive members. This latter point for four definite temperatures—viz. 20, 37·8, 50, and 98·9° C.—is given in Fig. 10, and it is interesting to note the great effect of chain length in change of viscosity with respect to temperature. For amylbenzene the change of viscosity between 20° and 98·9° C. (left-hand side of diagram) is not more than 1 centistoke, whilst for tetradecylbenzene (right-hand side of diagram) it is more than 7 centistokes. Further, the coefficient of change of viscosity with chain

length is smaller at the higher temperatures and increases with decreasing temperature.

The carbon and hydrogen determinations are as follows :—

$C_5H_{11}.C_6H_5$	C, 89·09 (Theory 89·11) H, 10·86 (Theory 10·89)	$C_9H_{19}.C_6H_5$	C, 88·05 (Theory 88·15) H, 11·78 (Theory 11·85)
$C_6H_{13}.C_6H_5$	C, 88·91 (Theory 88·81) H, 11·30 (Theory 11·19)	$C_{12}H_{25}.C_6H_5$	C, 87·70 (Theory 87·72) H, 12·37 (Theory 12·28)
$C_7H_{15}.C_6H_5$	C, 88·54 (Theory 88·55) H, 11·58 (Theory 11·45)	$C_{14}H_{29}.C_6H_5$	C, 87·62 (Theory 87·50) H, 12·50 (Theory 12·50)

Summary.

(1) Six *n*-alkyl phenyl ketones (alkyl group: C_4, C_5, C_6, C_8, C_{11}, and C_{13}) were prepared by Friedel–Crafts' reaction in carbon disulphide solution at 5–10° C. Yield of the products decreases on ascent of the series (80–69 per cent.). The ketones can only be obtained in pure condition by repeated distillations *in vacuo* and repeated recrystallizations. The quantities of ketones obtained ranged from 800 to 1500 grams.

(2) Change of density of the ketones is strictly linear with respect to temperature. Increase of the chain length decreases the density.

(3) Change of refractive index of the ketones is also linear with respect to temperature. Increase of the chain length decreases the refractive index. Still the influence of the absorption bands of the phenyl and carbonyl groups is persistent. Good agreement was obtained between observed values and calculated values for molecular refractivity.

(4) Three derivatives (semicarbazone, oxime, and 2 : 4-dinitrophenylhydrazone) were prepared for each ketone, and the melting points are recorded. The melting points of the derivatives show irregularity on ascent of the homologous series; the melting points of the derivatives plotted against the number of carbon atoms do not give a smooth, but an irregular, curve.

(5) Boiling point of the ketones increases on ascent of the series, but the melting point is irregular, and it is necessary to consider high (C_8) and higher members before any sign of regularity appears.

(6) Six corresponding *n*-alkylbenzenes (alkyl group: C_5, C_6, C_7, C_9, C_{12}, and C_{14}) were obtained by hydrogenating the ketones. Hydrogenation was effected by the Clemmensen's and the palladium catalytic methods. Clemmensen's method gives a poor yield (39–58 per cent.). Excellent yields have been obtained by the catalytic method (92–95 per cent.). The ketones used should be pure and sulphur free in both cases.

(7) The experimentally determined linear relationship between density and temperature for all the six hydrocarbons is given. Increase of chain length decreases the density for temperatures below 50° C.; the effect diminishes when the temperature is increased and at 70° C. the hydrocarbons have practically the same density. At still higher temperatures (above 90° C.) the reverse is the case.

(8) Change of the refractive index of the hydrocarbons is also linear with respect to temperature. Increase of chain length causes a decrease in refractive index. Good agreement between observed and calculated

values for molecular refractivity was obtained, especially when Hulst's values of atomic refractivities for carbon and hydrogen were used.

(9) Both boiling points and melting points increase on ascent of the series.

(10) Increase of chain length increases the viscosity of the *n*-alkylbenzenes. This increase is more enhanced for the higher members than for the lower, and for the lower temperatures than for the higher.

(11) Critical solution temperature in aniline increases as the chain length increases.

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OBITUARY.

SIR ROBERT ABBOTT HADFIELD.

Sir Robert Abbott Hadfield, Bart., died at his home in Kingston, Surrey, on 30th September. He was an Honorary Member of the Institute, having been elected in 1929 in recognition of his distinguished services to metallurgy, and in particular for his discovery and development of the special alloy steels which find extensive application in petroleum technology.

Sir Robert, who was chairman and managing director of Messrs. Hadfields, Ltd., Sheffield, and occupied a prominent position in industrial circles for many years, was born in Sheffield on 28th November, 1858. He entered the works of his father, a small steel foundry at Attercliffe, and pursued a course of practical training in metallurgy and engineering. Early in life he was attracted by the possibilities of alloy steels, and at the age of 22 had not only produced manganese steel, but had studied its heat treatment. On the death of his father in 1888 Sir Robert took over the management of the Attercliffe works. The company rapidly expanded, and new works were commenced in 1897 at Tinsley, Sheffield. Sir Robert continued as chairman of the company throughout his life, maintaining a close personal interest in all its activities until a year or two before his death.

In the field of metallurgy Sir Robert will chiefly be remembered for his researches on manganese steel; on low-hysteresis silicon steel for transformers and electrical plant; and for heat-resisting steels of various types. In the course of his researches he gathered round him a team of metallurgists, chemists and engineers who, under the inspiration of his leadership, proved distinguished and energetic co-workers. In collaboration with Dr. S. A. Main, Sir Robert presented a paper on "The Use of Steel in the Oil Industry with a Special Reference to Heat-Resisting Steels" to the Second International Drilling Congress in Paris, 1929.*

During his long career Sir Robert presented over two hundred contributions to the Proceedings of learned and technical societies and institutions in this country and abroad. His earliest papers were the classical researches on iron–manganese and iron–silicon alloys, presented to the Institution of Civil Engineers and the Iron & Steel Institute in 1888 and 1889. Subsequent papers dealt with alloys of iron with chromium, aluminium, tungsten and copper, with hardness and impact testing. In later years he devoted considerable attention to the history of metals, and it was largely owing to his patient historical research that the metallurgical work of Faraday was made known to the world at the time of the Faraday Centenary in 1931.

Sir Robert was knighted in 1908 and created a baronet in 1917. He was elected F.R.S. in 1907, and received the degrees of the Universities of Oxford, Sheffield, and Leeds. He was awarded the Albert Medal of the Royal Society of Arts in 1935. Decorations of the highest order were conferred upon him by governments and scientific bodies all over the world—in the United States, France, Norway, Sweden, Italy, Japan, and U.S.S.R.

* *Journ. Inst. Pet. Tech.* 1929, **15**, 611–633.